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Polypropylene-based wood -plastic composites reinforced with nanoclay

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**POLYPROPYLENE-BASED WOOD-PLASTIC COMPOSITES REINFORCED WITH
NANOCLAY**

by

Shu-Kai Yeh

**Dissertation submitted to the College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Chemical Engineering**

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**Morgantown, West Virginia
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**Keywords: PP, wood plastic composites, twin screw extrusion nanocomposites, TGA,
water absorption, and mechanical properties
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Abstract

POLYPROPYLENE-BASED WOOD PLASTIC COMPOSITES REINFORCED WITH NANOCLAY

by Shu-Kai Yeh

The increase in modulus of polypropylene (PP) upon addition of montmorillonite (MMT) makes PP-based polymer nanocomposites (PNCs) ideal matrix materials for wood/plastic composites (WPCs) for decking, railing, roofing and siding applications, among others. In this work, the influence of maleated PP (that is used both as a coupling agent for WPCs and as a compatibilizer for the PNC) on increasing the modulus of extruded and injection molded PP-based WPCs is investigated. Also examined are the effects of the sequence of compounding steps and the use of different processing conditions. The improvement in mechanical properties is examined by varying the amount of wood flour (WF), montmorillonite (MMT) and maleated PP in the WPCs and is explained with the help of available composite modeling theories. It is also related to the composite morphology with the help of scanning and transmission electron micrographs. The results indicate that by proper compounding, adding 2wt% to 4wt% of nanoclay in the matrix of the WPCs could significantly increase the modulus of WPCs without sacrificing the strength of WPCs. This increase in modulus can be explained with the help of a modified rule of mixtures.

The rate of water absorption of PP-based wood plastic composites was measured to determine if the rate of water absorption of WPCs is affected by the processing variables such as screw speed, residence time and screw geometry. The results indicate that a longer residence time and high screw speed both help reduce the rate of water absorption of WPCs by 10 to 40% without affecting in mechanical properties. The lower rate of water absorption seems to correlate with smaller particle sizes and a reduction in WPC density.

When wood was first compounded with the polymer and clay was added in the second step, it was found that WPC modulus was increased without significant reduction in strength. Furthermore, even in the presence of clay, the rate of water absorption could be kept at the same level as in the absence of clay when proper compounding procedures were used.

DEDICATION

To my parents, brothers and friends who support me in this long run.

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LIST OF SYMBOLS, ABBREVIATIONS, OR NOMENCLATURE

1. E_c : Modulus of composites
2. E_f : Modulus of fiber
3. E_m : Modulus of matrix
4. V_f : Volume fraction of fiber in the composites
5. V_m : Volume fraction of matrix in the composites
6. ν_m : Poisson ratio of the matrix
7. α : Aspect ratio of the inclusion
8. ABS: Acrylonitrile Butadiene Styrene
9. HDPE: High Density Polyethylene
10. PP: Polypropylene
11. PS: Polystyrene
12. PVC: Poly vinyl chloride
13. MMT: Montmorillonite
14. WF: Wood flour
15. WPC: Wood plastic composites

CHAPTER 1: INTRODUCTION

1.1 Wood Plastic Composites (WPCs)

Wood is a common engineering material which has many applications including construction, decking, fencing and furnishing. Different wood species have been widely used because they are abundant in the natural environment and cheap. However, wood, like other natural products can be attacked by termites and degraded by fungus. Additionally, the dimensional stability of wood is strongly affected by the relative humidity in the environment. Because of these disadvantages, wood has to be periodically treated with some hazardous chemicals like chromated copper arsenate (CCA) to prevent degradation; CCA-treated wood was phased out of the building products market by the Environmental Protection Agency (EPA) at the end of December 2004 [1]. This law, consequentially, promotes the growth of alternative materials such as wood plastic composites.

The term wood plastic composites usually means compounding equal amounts of wood flour (WF) or particulates with thermoplastic polymers such as polypropylene (PP), polyethylene (PE), polystyrene (PS), poly vinyl chloride (PVC), or acrylonitrile-butadiene-styrene (ABS). Since the wood content in the polymer matrix is high, the appearance and smell of WPCs are similar to natural wood. Wood plastic composites were first produced in the United States in 1983. Among others, American Woodstock, now part of Lear Cooperation in Sheboygan, Wisconsin, started to compound PP-based wood plastic composites using Italian extrusion technologies. The compounded products were extruded in the shape of flat sheets and then formed into different shapes for interior automotive paneling [2].

Wood plastic composites can be produced by different processes depending on the consumer's need. Since the major markets for WPCs are decking, railing, fencing and siding, 97% of wood plastic composites are produced by profile extrusion [3]. WF is well accepted by plastic processors as a filler because it is cheap and readily available. The stiffness and strength of plastics can be increased by adding WF as a filler. Wood also causes less abrasion to an extruder than mineral fillers such as glass fiber and talc. Since wood cools faster than plastics, there is no need for "calibrating" to shape a part of WPC lumber [2]. On the other hand, for construction related products such as windows, door sills, railing spindles, and railing post skirts and caps and non-construction related WPCs include automotive parts and furniture components and these have been developed by injection molding industries. The ability to use recycled plastics in WPCs is an economic incentive, and there is a general perception that WPCs are quite durable and resistant to decay since the wood particulates are expected to be completely encapsulated by plastic.

The market of WPCs is expected to grow at a rate of 15%~20%/yr until 2010, faster than both plastics and building products. The demand for wood and natural fiber composites in North America and Europe has increased by a factor of 12 from 1995 to 2002. While the addressable market segment of WPCs in the United States was 26 billion lbs in 2004, market penetration was only 5%. In 2004, WPCs penetration in decking and railing was 15%. The penetration rate is expected to grow to 25% by 2009. The market for decking and railing is also expected to increase from 4.3 billion to more than 5 billion USD from 2004 to 2009. Decking products occupied 53% of total WPCs volume. All of these data indicate that the market for WPCs is experiencing rapid growth and will keep a growth rate of 20% until 2010. Among all of the plastics, high density polyethylene (HDPE) is the

major plastic used in WPCs. PE-based WPCs occupy 83% of the market, followed by PVC (9%) and PP (7%) and other plastics (1%). Ten suppliers account for 70% of the market supply in the United States. Trex Company Inc. is the number one player in this market and possesses 22% of market share [4, 5].

The properties, processability and rate of production of wood plastic composites can be improved drastically if proper additives are used. Plastics, such as HDPE and PP, tend to absorb much less moisture than wood in the natural environment. Therefore, WPCs are less affected by moisture and possess better dimensional stability and fungus/termite resistance than solid wood because wood particulates are encapsulated by the polymer matrix. Since thermoplastic polymers like PP and HDPE are non-polar (hydrophobic) materials while wood particulates are polar (hydrophilic) materials, there is a high probability of obtaining poor adhesion between wood and polymer resulting in low tensile and flexural strengths of the WPCs [6]. In order to improve the adhesion between wood and plastics, maleic anhydride grafted polymers are generally introduced as a compatibilizer to improve the strength of WPCs. In addition, when the adhesion of WF and plastics is enhanced, the rate of water absorption also decreases in the presence of the coupling agent.

The production rate of WPCs can be substantially increased when lubricants such as zinc stearate or fatty acids are added in the compounding process. Lubricants help to suppress edge tearing and melt fracture phenomena happening in the extrusion process. Generally, the density of WPCs is higher than that of solid wood and this limits the applications of WPCs. The density of WPCs can be reduced by as much as 30% by adding blowing agents that make the density of WPCs similar to real wood. Foaming also helps a

manufacturer save on material cost. The fungus resistance of WPCs is improved by adding biocides. WPCs can be colored easily by adding colorants. Adding a UV stabilizer can improve the UV stability and weatherability of WPCs. Since the major applications of WPCs are in construction, flammability of WPCs is another concern and flame retardants are used for the purpose. Antioxidants are also applied here to prevent polymer from degrading during the compounding process. Finally, some fillers such as glass fiber, talc, calcium carbonate and nanoclay are recommended as the second filler in the WPCs to improve mechanical properties and creep resistance. Indeed, the desired properties of WPCs can be achieved with a combination of different additives [7]. Overall, a coupling agent, lubricant and blowing agent are the additives which attract more attention in the WPC industry. The functions of different polymer additives used in WPC are listed in Table 1-1.

Table 1-1 Typical polymer additives used in wood plastic composites

Additives	Function
Coupling Agent (compatibilizer)	Strength improvement, water absorption rate reduction
Lubricant	To increase production rate by reducing extrusion instabilities
Blowing Agents	Density reduction
Biocides	Fungus resistance
Colorants	Color
UV Stabilizers	UV stability
Antioxidants	Polymer degradation prevention
Flame retardant	Flame retardancy

These days, the applications of WPCs are limited by material performance. The reason for this is that while the flexural strength of plastics used in compounding WPCs is

approximately 40 - 80MPa, the flexural modulus is only about 1.5 – 2.5GPa [8]; the corresponding values for natural wood can be as high as 80MPa for strength and 9GPa for the modulus. Thus, any combination of WF and plastic will lead to WPC flexural and tensile moduli that are significantly lower than those of natural wood. A deck constructed out of WPC, therefore, will flex much more than an identical wood deck for the same load, and this is undesirable. Additionally, more research needs to be done on the long-term material behavior such as weather durability and creep. The flame retardancy of WPCs is especially important in some states like California which have regulations in this regard. Material performance of WPCs today has already met builder acceptance as a non-structural material for decking. With more and more research being done in this area, it may be possible to use WPCs as structural materials in the future (Figure 1-1). Therefore, product evaluation standards of wood plastic composites have to be established to meet the consumer's demand and safety requirements. ASTM international has also noticed this new class of material and released two new standards, D7031 and D7032, in 2004 [9, 10]. These standards are published under ASTM committee D07, "Structural Wood and Wood-Based Products Standards".

Figure 1-1 The relationship of natural fiber composites performance and timeline [11]

1.2 Polymer Nanocomposites

Like all other composites, a “nanocomposite” is defined as a two or more phase system where one phase is dispersed into the other phases. Although polymer-clay interactions have been studied during the sixties and the early seventies, the concept of polymer-clay nanocomposites was not proposed until the early nineties [12]. The concept of polymer-layered silicate nanocomposites was proposed by Toyota in the early 90’s using Nylon-6 as the polymer matrix. The first report from the Toyota research group pointed out that adding a very small amount of layered silicates to nylon leads to pronounced improvements in thermal and mechanical properties. These improvements include high moduli, increased strength, enhanced heat distortion temperature, decreased gas permeability, and reduced flammability [13]. These features attracted enormous interest from both academia and industry. Nowadays, efforts are being made globally to produce polymer-layered silicate nanocomposites using all kinds of polymers.

Among the numerous layered silicates tested, montmorillonite is the most effective nanofiller because it has a plate-like structure and a high aspect ratio to give an enormous surface area. In addition, montmorillonite is abundant in nature. A montmorillonite platelet usually includes aluminum or magnesia atoms in the center of an octahedral sheet which is fused with two external silica tetrahedron layers. This sandwich structure is called a unit layer. The idealized structure of a montmorillonite unit layer is given in Figure 1-2. The thickness of a unit layer is around 1 nanometer and the lateral dimensions of the platelet range from several hundred nanometers to several thousands of nanometers. Typically,

though, clays are composed of many such layers stacked in parallel to one another and held together by Van der Waals forces.

In many types of clay, the lateral Si^{4+} atoms shown in Figure 1-2 are partly replaced by trivalent atoms such as Al^{3+} and/or the central Al^{3+} atoms are also partly replaced by some divalent atoms such as Fe^{2+} and Mg^{2+} . Because of that, the lack of positive charges on the clay platelet surface is usually compensated by adsorbing Na^+ and Ca^{2+} ions present in water. These cations can be exchanged by other cations that are present in solution. This property of clay makes it possible to replace inorganic cations on the unit layer surface with organic cations by ion exchange mechanism, and this makes the clay develop an affinity for an organic phase such as polymer. The typical cations used in clay modification include: primary, secondary, tertiary and quaternary alkylammonium or alkylphosphonium cations. These cations act as surfactants and lower the surface energy of the inorganic host. Therefore, the wetting characteristics of the polymer matrix are improved, and this results in a large interlayer spacing. In some cases, the cations on the surface of the layered silicate can initiate the polymerization of monomers to improve the bond strength between the layered silicate surface and polymer [13].

Figure 1-2 Idealized structure of montmorillonite. [12]

Clay-filled polymers are classified as one of three types of composites based on their morphology: conventional composite, intercalated composite or exfoliated / delaminated composite. This classification is determined by the interaction of polymer and clay. When the polymer chains are not able to penetrate through the gaps between the unit clay platelets, the stacks of clay remain in the original aggregates, and this is known as a conventional or macroscopic composite. In some other polymer-clay composites, polymer chains are intercalated into unit clay platelet gaps but the platelets are still not able to exfoliate in the polymers. This type of morphology is called intercalated composite. When the clay platelets are randomly dispersed into polymers and the gaps between each platelet are expanded, this structure is called exfoliated or delaminated composite. A schematic diagram of these morphologies is shown in Figure 1-3. Among these three types of morphologies, exfoliated morphology is believed to give the maximum benefit because the montmorillonite clay has a high surface area (around $750 \text{ m}^2/\text{g}$) [14]. Property enhancement is decided by the molecular level interactions between clay surface and polymer. Since montmorillonite clay platelets present the largest surface area in exfoliated morphology, the property enhancement of polymer nanocomposite is very significant even with very small clay loading.

Figure 1-3 Types of nanocomposite morphologies. [12]

In the research described here, improving the modulus of WPCs will be the major issue and the problem can be addressed in one of two ways: one may either increase the percentage of wood in WPCs or one may increase the modulus of the matrix polymer. The concept of increasing the modulus of the matrix is relatively more attractive. In this regard, the properties of polymer nanocomposites containing layered silicates make them good candidates for this purpose. Compared to other mineral fillers such as glass fiber and talc, MMT possesses similar density but much higher modulus. An example from Nylon-6 clay nanocomposites is illustrated in Figure 1-4. Adding 6.5wt% of layered silicate in Nylon-6 could double the modulus of the polymer; by contrast, three times this amount of glass fibers is needed to accomplish the same increase. The modulus of MMT as determined by ultrasonic pulsing method is 178GPa [15]. Furthermore, recent studies indicate that the modulus of MMT can be as high as 400GPa based on molecular dynamic simulations [16].

Figure 1-4 Comparison of the reinforcement of nylon 6 by organically modified montmorillonite (nanocomposites) and glass fibers. Nanocomposite filler concentration is based on the wt% of inorganic montmorillonite [15].

The high surface area of montmorillonite clay plays an important role in property enhancement of polymer nanocomposites. In both exfoliated and intercalated nanocomposites, dispersed nanoclay platelets create a tortuous structure inside the polymer matrix. The effective diffusion path for a diffusing molecular is longer. Therefore, polymer nanocomposites have very good diffusion barrier properties for liquid and gas (see Figure 1-5) [17].

Figure 1-5. Different diffusion paths in polymer and polymer nanocomposites [17].

1.3 Project Details

In this study, WPC pellets are made by twin screw extrusion. The extruded pellets are then injection molded into samples for mechanical testing. PP is used as the polymer matrix in these experiments. There are several objectives which are achieved here:

- (1) Increasing the modulus of PP-based WPCs by adding nanoscale fillers.
- (2) Reducing the rate of water absorption of PP-based WPCs with and without nanoclay by changing the process variables

In the first part of the study, the mechanical and thermal properties of PP homopolymer / maple WF wood-plastic composites are investigated extensively. WPCs containing different weight percentages of WF, nanoclay, and coupling agents are compounded by a Leistritz Mirco-27 lab extruder using both co/counter rotation modes. The impact of process variables on the mechanical properties of WPCs are also discussed. These key variables include: feeding rate, residence time and screw speed and all of these

variables are related. The rheological properties of WPCs are studied using a capillary rheometer.

In this thesis, the following aspects were studied:

1. The effect of coupling agent amount on mechanical properties of PP-wood and PP-nanoclay-wood plastic composites
2. The effect of process variables including screw speed and feeding rate, screw geometry and residence time on the mechanical properties and water absorption rate of wood plastic composites.
3. The effect of wood content and nanoclay content on the mechanical properties of PP-based wood plastic composites.
4. The effect of different compounding procedures on the mechanical properties of nanoclay reinforced WPCs.
5. Modeling the modulus of wood plastic composites by theories such as the modified rule of mixtures and the Halpin-Tsai equation.

CHAPTER 2: LITERATURE REVIEW

2.1 Wood Plastic Composites and Additives for WPCs

2.1.1 Wood Fibers

Wood fibers usually contain cellulose, hemi-cellulose, pectin, lignin, water soluble ingredients, and wax [18]. The actual composition of these materials in wood fibers, though, varies from species to species. Here, water soluble constituents and wax are considered as extractives since cellulose, hemi-cellulose, and lignin are considered to be the basic components with regard to physical properties [18]. Generally, more than 50% of wood fibers are cellulose. The chemical structure of cellulose is shown in Figure 2-1. The hydroxyl groups on the cellulose make WF hydrophilic.

Figure 2-1 Chemical structure of cellulose [18]

The moduli of cellulose-based materials are very different from each other. For example, the Young's modulus of solid wood is around 10GPa. By proper pulping process the modulus of a single pulp fiber can be as high as 40GPa. Microfibrils can be separated from pulp fibers after mechanical disintegration and hydrolysis. The modulus of microfibrils is around 70GPa. Finally, the modulus of cellulose nanocrystals is obtained by theoretical calculation, and this could be as high as 250GPa [18]. From the same literature,

the moduli values of wood fibers range from 10 to 90GPa [18]. From these numbers, we can say that it is reasonable to compound WF with plastics to increase the modulus of resins of interest because the modulus of wood fibers (40GPa) is much higher than that of most plastics. The high moduli of wood fibers make these good candidates as plastic reinforcements.

As mentioned earlier, the properties of natural fibers vary from species to species and region to region. Additionally, WF usually contains 6 ~ 8wt% of water and needs pre-drying before processing. This can cause problems in utilization and processing of wood plastic composites. The main problems related to processing of wood plastic composites are: [19]

- ◆ Region and species variations in the quality of raw material
- ◆ Compatibility limitations due to compounding hydrophilic WF with hydrophobic matrix
- ◆ Limited thermal stability during processing. WF can not be processed above 200°C or WF will be burned and change the appearance and mechanical properties of WPCs [20]
- ◆ Shape deviation of the component caused by the swelling of WF

Among the problems stated above, the quality variation and thermal instabilities are intrinsic problems associated with natural materials. Nevertheless, the compatibility of WF with thermoplastics and the shape deviation caused by swelling of WF can be solved by proper modification of the surface of WF. In this way, the strength of WPCs can be improved, and the rate of water absorption of WPCs can be reduced.

In summary, the high modulus of wood fibers makes them good candidates as plastic reinforcements. However, the thermal instability nature of WF places an upper limit on the processing temperature. Other intrinsic properties such as quality variation and shape irregularity also limit the applications of WF. The most important problem, however, is the hydrophilic nature of WF. Due to this, water uptake swells WF and affects the dimensional stability of WPCs. Moreover the fungus susceptibility of WPCs increases, too.

2.1.2 Coupling Agents

As can be seen from Figure 2-1, the chemical structure of cellulose contains enormous amounts of hydroxyl groups. These hydrophilic hydroxyl groups absorb water molecules easily and swell the wood fiber. The theoretical swelling pressure for wood can be as high as 1630 atm [21], and this pressure can cause fiber-matrix debonding in the wood plastic composite. A schematic illustration of the swelling process is depicted in Figure 2-2 [19]. As shown, the hydroxyl groups on different wood fibers form hydrogen bonds and, as a result, WF aggregates easily.

The dispersion of WF and fiber wetting can be improved by modifying the surface of WF. The use of coupling agents results in reaction with the hydroxyl groups on the surface of WF, and this disrupts the hydrogen bonds between wood fibers.

Figure 2-2 Schematic illustration of the wood fiber swelling process [19]

The coupling agents which are used to compatibilize WF and polymer matrix are those that possess methanol groups, isocyanates, triazine, and organosilanes [18]. Bledzki et al., consider polymethylene-polyphenyl isocyanate (PMPPIC) as the most useful coupling agent because it forms strong covalent bonds with the wood-OH groups, resulting in a urethane structure. The addition of PMPPIC to the matrix not only improves the tensile strength, but the elongation at break, too [19]. However, maleic anhydride grafted polymer is the most commonly used coupling agent in the WPCs industry today because of its availability and its ability to improve the strength of WPCs. A schematic diagram depicting the reaction between maleic anhydride and WF surface is shown in Figure 2-3.

Figure 2-3 Esterification of cellulose fibers with maleic anhydride [18].

Encapsulating WF with chemicals such as polypropylene grafted maleic anhydride (PP-g-MA) in PP-based WPCs produces an insulation layer on the surface of WF and also makes them hydrophobic. The hydrophobic nature of PP-g-MA treated wood can be proved by conducting Takase's test [22]. It is conducted by shaking WF in an ether/water mixture. After separation of the two phases, untreated WF sinks in the water phase while PP-g-MA treated WF floats to the interface. Moreover, PP-g-MA treated WF can be extracted from composites by dissolving the matrix using hot xylene and Soxhlet extraction to remove the modifier which is not covalently bonded to the WF surface and to destroy the hydrogen bonds which may be formed between WF and PP-g-MA. The result shows that after these treatments, PP-g-MA treated WF is still hydrophobic. It means that PP-g-MA is covalent bonded to the surface of WF and makes WF hydrophobic. In this way, the rate of water absorption of WPCs is decreased. However, it has been determined that the number of hydroxyl groups present on the surface of WF is only around 1% of the total number of hydroxyl groups in cellulose [23, 24]. Thus, modifying the fiber surface with PP-g-MA to

prevent water uptake works well in the case of glass fibers, which contain hydroxyl groups only on the surface. But this is not the case for natural fibers which also contain hydroxyl groups in the bulk. Therefore, unmodified hydroxyl groups existing in the cellulose are accessible to water molecules which are small enough to enter cellulose wall pores (40 Å – 40 µm) [25]. The experiments done by Viksne et al., [26] prove that water uptake by WPCs primarily affects the modulus of WPCs but not the strength. In practice, WF made from different species of wood such as Maple, Oak (hardwood) and Pine (softwood) are used to compound wood plastic composites. Other than WF, long wood fibers and wood chips have also been used [26 – 38], but WF is still the most commonly used form because of the ease of processing with a twin screw extruder.

In summary, coupling agents are added to wood plastic composites to increase their strength and to decrease the rate of water absorption. Maleic anhydride-based coupling agents are popular in the industry because of their effectiveness and ready availability.

2.1.3 Lubricant

A lubricant is another common additive which is used extensively in wood plastic composites extensively. The viscosity of filled polymer increases as the filler content increases. The rapid increase in viscosity with added WF, especially at low shear rates, is relevant to the phenomenon of melt fracture that is often observed during extrusion of WPCs, since this limits production rates. In this case, lubricants are usually introduced in the WPCs as additives to reduce the melt fracture and to increase the production rate. The typical lubricants applied in the PP/WF system are ethylene bisstearamide (EBS) and zinc stearate (ZnSt). The chemical structure of EBS and ZnSt can be seen in Figure 2-4.

However, experiments done by Harper et al. [39] show that ZnSt reacts with PP-g-MA, and this reaction can destroy the bonding between PP-g-MA and WF. Moreover, microscopic pictures show that PP / PP-g-MA blends usually crystallize on the surface of WF, and these crystals may improve the strength of WPCs. Indeed, the addition of ZnSt impairs the crystalline growth on the WF surface and thus negates the effect of PP-g-MA [39]. To verify the effect of lubricant on the mechanical properties of WPCs, three batches of WPCs containing no additives, 4wt% PP-g-MA to WF and 4wt% PP-g-MA plus ZnSt/EBS lubricant, respectively were compounded using a Leistritz twin screw extruder at WVU and the results are shown in Figure 2-5. As can be seen from Figure 2-5, the effect of the coupling agent is negated in the presence of lubricant. Recently, several chemical companies have developed lubricants which have no negative effects on coupling agents. These lubricants are usually ester-based lubricants and contain no metal ions such as zinc.

In summary, the addition of lubricants reduces melt fracture and increases the production rate of WPCs. However, it often negates the effect of the coupling agent. It is worthwhile to apply recently developed lubricants which do not negate the effect of coupling agents.

Figure 2-4 The chemical structure of (a) ethylene bisstearide (EBS) and (b) zinc stearate (ZnSt) [39]

Figure 2-5 The negative effect of lubricant to coupling agents in 50wt% maple WF / PP system

2.1.4 Melt Fracture

Melt fracture usually happens during extrusion when the polymer melt exceeds a critical shear stress or shear rate. A typical flow curve showing the regimes of instability for a linear polymer melt is shown in Figure 2-6. Melt fracture manifests itself as irregularities on the surface of the extrudates. This is very important especially when 97% of the wood plastic composites are made by profile extrusion. Therefore, it is important to reduce the melt fracture phenomenon during extrusion.

Figure 2-6 Typical flow curve and regimes of instability for a linear polymer melt [40].

There are several ways to reduce melt fracture [40]:

- Streamlining the die flow channel
- Reducing the Shear Stress in the land region (operating below the critical shear stress for melt fracture)
- Using a processing aid
- Using “super extrusion” (operating above the critical shear stress for melt fracture)
- Ultrasonic vibration

In addition, the following methods are applied to reduce the shear stress in the die land region:

- Increasing the die land temperature

- Opening up the die and land region (increasing the die gap)
- Reducing the extrusion rate
- Using a process aid (external lubricant)
- Increasing the melt temperature
- Reducing the polymer melt viscosity
- Using a more shear-thinning plastic

Among these methods, using process aids such as lubricants and increasing the die land temperature are the two methods which can be done easily. Therefore, lubricants are usually added to the WPCs to reduce melt fracture and to increase the production rate. This is especially true for ABS-based WPCs since the processing temperature of wood plastics is limited to 200°C which has been mentioned in Chapter 1 [20]. If we can understand the rheology of wood filled polymers melts better, it will also help us understand the melt fracture phenomenon. As early as the 1980s, Maiti et al. [41, 42] investigated the rheological behavior of wood filled PP. Starting from 2003, fundamental research on the rheological behavior of wood filled HDPE has been done by Li et al. [43 – 46] using a capillary rheometer. Chastanger adopted Li's idea but used an on-line measurement method to analyze the rheological behavior of wood filled ABS later [47].

In summary, melt fracture can be reduced by increasing the die temperature and by adding lubricants in the formulation. Increasing the screw rotational speed in an extruder promotes the shear thinning behavior of polymer melts, and therefore melt fracture is suppressed, too.

2.2 Plastics Used to Formulate Wood Plastic Composites

Because WF will be burnt when processing temperature is above 200°C, the plastics used as the matrix in WPCs are limited. High density polyethylene (HDPE), polypropylene (PP) and polyvinyl chloride (PVC) are the most common matrix materials in WPCs. This is because the price of these three resins is lower than that of other engineering plastics and their processing temperature is lower than 200°C. Since the melting point of HDPE (134°C) is lower than that of PP (168°C) and PVC (glass transition temperature = 90°C), it commands more than 80% of the WPC market [4, 5, 48].

PVC is another common plastic used in WPCs. Unlike HDPE and PP, the molecular structure of PVC is such that it is hydrophilic. Therefore, PVC is more compatible with WF. Additionally, PVC contains chlorine which acts as a flame retardant in plastics. Because of this, the flammability of PVC-based WPCs will be less than that of PP or HDPE-based WPCs. However, since the materials which contain halogen can be toxic the market of PVC-WPCs is not as large as those for polyolefin-based WPCs.

PP occupies a prominent role in the WPC market. The advantage of PP is that it possesses slightly higher stiffness than HDPE [48]; the price is comparable to HDPE, and the heat deflection temperature of PP is higher than HDPE. PP-based WPCs simply offer another choice for WPCs [49].

Currently, other plastics which have processing temperatures lower than 200°C such as ABS and PS have not been widely used in WPCs. Due to its limited ductility (impact strength < 35 J/m and elongation at break < 2.5%), polystyrene (PS) is not a good matrix material for WPCs [48]. Note that fillers which exist in the polymer act as stress

concentrators and can decrease the impact strength of plastics. ABS may have more opportunities in WPCs since it is hydrophilic and its mechanical properties are much better than those of HDPE, PP or PVC. The problem here is that the price of ABS is higher than that of the other plastics. Nevertheless, the price of recycled ABS is low. The current price of recycled ABS is even lower than that of recycled polyolefin. The National Safety Council predicts that there will be 680 million computers obsolete within the next few years. According to London-based Economist Intelligence Unit, the waste from these computers contains 4 billion pounds of plastics [50]. Most of these plastics are ABS, HIPS and ABS/PC blends. These waste plastics will provide a new material stream for WPCs and make the price of ABS-based WPCS be comparable with current WPCs.

2.3 Preparation of Polymer Nanocomposites

In chapter 1, the structure of montmorillonite and the types of morphology of polymer nanocomposites were reviewed. In this section, the preparation of polymer nanocomposites will be reviewed. There are three different ways to prepare polymer nanocomposites: 1. Intercalation of polymer or pre-polymer from solvent / aqueous solution, 2. In situ intercalative polymerization method and 3. Melt intercalation method [13].

In the first method, polymers are dissolved in water or in an organic solvent such as xylene and toluene and then mixed with organoclay. Polymer chains can be successfully intercalated into the clay galleries. After that, the organic solvent or water is evaporated and intercalated nanocomposites are obtained. This method was first adopted in 1992 by Aranda et al. using polyethylene oxide as base polymer [54]. This method is not popular because it needs large amounts of organic solvent, and this is not environmentally friendly.

In the second method, the galleries of layered silicates are swollen using liquid monomer or a monomer solution [13]. The first report of polymer nanocomposites prepared by in situ polymerization methods was in 1990 by Toyota using nylon-6 as the base polymer [55]. By this technique, monomer could penetrate through the clay galleries. After polymerization starts, the clay platelets expand and exfoliated polymer nanocomposites are obtained.

In the melt intercalation method, organoclay is directly melt intercalated with polymer melts by polymer blending. This method is of great interest to the polymer industry since it does not use any organic solvents and is compatible with current industrial processes such as extrusion. Therefore, the melt intercalation technique has become the standard method for the preparation of polymer nanocomposites [13]. This method was first adopted by Vaja et al. to prepare polystyrene-based nanocomposites in 1993 [56]. In a typical example, organoclay powders are dry blended with polystyrene. The mixtures are first pressed into pellets and heated up to 165°C under vacuum which is well above the glass transition temperature of PS to ensure polymer melting. The samples heated for various times are investigated by XRD analysis. The results are shown in Figure 2-7. As can be seen in Figure 2-7, after the samples endured for 0, 2, 5, 15 and 25 hours of heating, the X-ray diffraction (XRD) patterns of PS-nanoclay mixture became different. The XRD patterns of hybrids before heating (0 hours) indicate the original diffraction pattern of nanoclay. After 25 hours of heating, the peak progressively shifts to smaller angles. These patterns indicate that layered silicate platelets are intercalated with polymers after melt blending. The detailed information of how to characterize polymer nanocomposites by XRD and will be discussed in the next section.

Figure 2-7 Representative XRD pictures of PS / layered silicate hybrids heated to 165°C for various times. Asterisks indicate the position of the basal reflections from the pristine organoclay [56].

Polymer nanocomposites were first prepared by twin screw extrusion in 1999 by Liu et al. using commercially available Nylon 6. Previously, in situ polymerization techniques were applied to prepare nylon 6 / clay nanocomposites. Liu et al. [57] prepared nanocomposites with MMT content from 1 to 18wt%. The observations from XRD patterns and TEM pictures indicated that an exfoliated structure was obtained with MMT content less than 10wt%. When the MMT content increased to more than 10wt%, an intercalated structure was obtained. Their results also indicated that the exfoliated structure strongly influenced the crystallization behavior of nylon 6.

PP is one of the most used polymers today for making polymer nanocomposites. Because it does not have any polar group on the polymer chain, it is difficult to directly

intercalate PP chains into the galleries of layered silicates. Usuki et al. proposed a new approach to prepare PP-based polymer nanocomposites using a functional oligomer (PP-OH) [58]. Later on, the same group did further study to prepare PP polymer nanocomposites by melt blending of PP, a maleic anhydride grafted PP oligomer (PP-g-MA) and stearylammmonium modified clay using a twin screw extruder [59]. Two different types of PP-g-MA with different MA content and two types of organoclay were employed. A schematic representation of the dispersion process is shown in Figure 2-8. Polymer scientists are interested in grafting other functional groups onto the PP chains to improve the exfoliation of PP / clay nanocomposites. Mania et al. [60, 61] did a detailed study and found that functional groups including p-methylstyrene, maleic anhydride, styrene, and hydroxyl-containing styrene promote PP nanocomposites formation with dimethylditallowammmonium modified MMT. In addition, octadecylammmonium-modified clay also formed nanocomposites with propylene-b-methyl-methacrylate diblocks. Among these different functional groups, PP-g-MA is the most popular one because it was first proposed and is commercially available. Maleic anhydride group can be grafted onto other polyolefin polymers, too. Other polyolefin-based nanocomposites can be formed with the help of maleic anhydride [62].

Figure 2-8 Schematic representation of the dispersion process of organic modified clay in PP with the aid of PP-g-MA [13]

Several follow up studies on PP-based nanocomposite extrusions have been done by different research groups [51, 63 - 75]. Most of these studies focus on the effect of MA content and molecular weight of PP-g-MA. The ratio of PP-g-MA to organoclay [63], clay concentration [65 – 67, 72], the feeding location of PP or clay [66, 68] and processing variables such as processing temperature, feeding rate, screw rpm [65, 68, 70, 72] and screw design [51, 63, 66 68, 70, 74] have also been discussed. It is of interest to note that most of these references use commercial PP-g-MA from Crompton (now Chemtura) and

Eastman Chemical because of their availability. The properties of these different PP-g-MAs are listed in Table 2-1.

Table 2-1 Typical commercially available PP-g-MA polymers [65, 70, and 75].

Manufacturer	Trade Name	Melt Flow Index (g/10min) 2.16kg/190°C	Molecular Weight (g/mol)	Melting Point (°C)	MA content (wt%)
Crompton	PB3150	20	330000	164	0.5
Crompton	PB3200	115	120000	163	1
Crompton	PB3000	425	61000	161	1.2
Eastman	E43	1654	9100	153	4
Eastman	G3003	80 (230°C)	52000	158	0.8

Kim et al. [73] mixed PP of different viscosity, different PP-g-MAs and clay with different treatments in an internal mixer to examine the effect of matrix properties on the formation of polymer nanocomposites. Samples made with higher viscosity PP were considered to experience higher shear stress during mixing. They found that the viscosity is not the only factor to affect the exfoliation of nanocomposites. Other issues such as the MA content of PP-g-MA, and types of functional groups grafted on the clay also have to be considered. Svoboda et al. [65] proposed using a low feeding rate (2kg/hr) and high rpm (300rpm) to compound PP nanocomposites without specially designed screws. The mechanical properties of polymer nanocomposites, especially the elongation at maximum stress, are discussed extensively in this reference. These authors found that with increasing clay content, the modulus increased progressively but the impact strength and strain at maximum load first increased and then decreased. This is because it is not easy to exfoliate clay at high clay concentration, and the macro sized clay aggregates that form have a negative effect on the impact strength and strain at maximum load. In addition, samples compounded with high molecular weight and low MA content PP-g-MA possess better

mechanical properties. This result is consistent with other references [63, 66, 68, and 70]. Wang et al. [63] did a detailed study on the ratio of PP-g-MA to clay. Four different kinds of PP-g-MA were employed in the experiment using an internal mixer. The screw speed was controlled at 100rpm for 15 minutes and the PP-g-MA to clay ratio was controlled at 1, 2, 3, 4, 6, 8, and 10, respectively. Their results indicate that PP-g-MA of low MA content but high molecular weight (PB3150) provides high shear strength during mixing. The clay platelets are well exfoliated in the high molecular weight PP-g-MA which can be seen in Figure 2-9 (a). On the other hand, although higher MA content in the PP-g-MA is considered to be helpful to exfoliate clay platelets, the low viscosity of high MA content PP-g-MA (E43) can lower the shear mixing strength significantly. Thus, clay platelets may not be exfoliated. This can be seen from the XRD pattern of PP-g-MA clay nanocomposites in Figure 2-9 (b). This result is consistent with references 39 and 40 that a sample made with higher molecular weight PP-g-MA provides better mechanical properties. The authors conclude that clay could be well exfoliated whenever the PP-g-MA to clay ratio is larger than 3. The same group did follow up studies which focus on the feeding location of PP and clay in a twin screw extrusion process [68]. They found that feeding PP-g-MA and clay in the hopper and then introducing PP using a side feeder from a downstream location (barrel 4) could give better clay dispersion. Lee et al. [72] and Lee et al. [75] applied the same concept in their experiments. Ton-That et al. fed clay from barrel 5 because they believed that clay would be exfoliated better in polymer melts. A schematic diagram of hopper feed and side feed are shown in Figure 2-10. These different strategies adopted by different researchers indicate that exfoliating nanoclay in PP is still an area of active research and it is not easy to comment on which strategy is more effective.

(a)

(b)

Figure 2-9 (a) XRD patterns of PB3150/I.30 (clay) nanocomposites:(1) pure I.30, (2) 1/1 PB3150/I.30, (3) 2/1 PB3150/I.30, (4) 3/1PB3150/I.30, (5) 4/1 PB3150/I.30, (6) 6/1 PB3150/I.30, (7) 8/1PB3150/I.30, and (8) 10/1 PB3150/I.30.
(b) XRD patterns of E43/I.30 nanocomposites: (1) pure I.30, (2) 1/1 E43/I.30, (3)2/1 E43/I.30, (4) 3/1 E43/I.30, (5) 4/1 E43/I.30, (6) 6/1 E43/I.30, (7) 8/1 E43/I.30, and (8) 10/1 E43/I.30. [63]

(a) Hopper feed

(b) Side feed

Figure 2-10 Feeding location of PP, PP-g-MA and clay (a) Hopper feed, (b) Side feed [68]

A two step compounding process approach was adopted by Lee et al. [72]. A master batch containing equal amounts of PP-g-MA (MA content = 1wt%) and organoclay was compounded using a co-rotating twin screw extruder. It is worthwhile to note that an extremely low feeding rate (1kg/hr) and a high screw speed (280rpm) were adopted to make the master batch. After that, the master batch was diluted with PP to get PP-based polymer nanocomposites containing different amounts of clay.

Definitely, PP-g-MA can help the exfoliation of organoclay platelets. Researchers are interested in the amount of PP-g-MA which can be adsorbed by organoclay. Wu et al. proposed a method which was used to measure the adsorption isotherm of liquid-solid interface [71]. The treated organoclay was dispersed in xylene with an excess amount of pre-dissolved PP-g-MA to make the mixed xylene solution. The solution was put in a glass tube in an oil bath to maintain the temperature at 120°C for 4 hours. The samples were

agitated to ensure attainment of equilibrium adsorption. After 4 hours, the supernatant was taken out from the tube by suction. The leftover clay complex was dried and analyzed by thermogravimetric Analysis (TGA) to determine the amount of polymer that was adsorbed by nanoclay. The adsorbed PP-g-MA per gram of clay first increased linearly with the equilibrium concentration of PP-g-MA and then leveled off and reached equilibrium.

Instead of treating the surface of clay, Hasegawa et al. [76] developed a new process for directly compounding Na^+ -montmorillonite (untreated clay) with nylon 6 by a slurry process. Sodium montmorillonite-water slurry was injected from the down stream end of the extruder and blended with nylon 6. Then, water was removed through a vent (See Figure 2-11). XRD patterns and TEM observations indicated that clay platelets were exfoliated in the nylon 6 matrix and the properties of nylon 6/ Na^+ -MMT nanocomposites were almost equal to those of nylon 6 nanocomposites prepared by dry blending with organically treated clay. A schematic figure depicting dispersion of the Na^+ -MMT slurry into nylon 6 during compounding is shown in Figure 2-12.

Figure 2-11. Schematic figure depicting the compounding process for preparing nylon/clay nanocomposites using a clay slurry [76].

Figure 2-12 Schematic figures depicting dispersion of Na^+ -MMT slurry into nylon 6 during compounding [76].

The same concept was adopted by Kato et al. [69] to prepare PP-based nanocomposites using a twin screw extruder. Here, PP, PP-g-MA, Na^+ -MMT and octadecyl ammonium chloride (OTM) were fed into the hopper. Water was injected into the extruder downstream to carry out the slurry process. After that, water was removed through a vent and polymer nanocomposites were obtained (See Figure 2-13). Water evaporates when the temperature exceeds 100°C . Consequently, when water is injected into the extruder, a high pressure is needed to ensure that water exists in the liquid state to promote clay exfoliation. Therefore, the real challenge in this process is to keep the pressure above the level needed to prevent water evaporation. Therefore, sealing is needed to maintain the high pressure and keep water in a liquid state.

Figure 2-13 Schematic depicting dispersion of silicate layers of clay in PP during compounding by the extruder. [69].

One of the research goals in the present work is to compound nanoclay with wood plastic composites to enhance the stiffness of PP-WPCs. Some other properties such as foaming ability and flame retardancy are also improved with the addition of nanoclay. The research done by Park et al. [77] has proved that nanoclay improved the flame retardancy of metallocene PE-WPCs in a horizontal burning test [78]. In addition, density of foamed metallocene PE-WPCs decreases by adding 5wt% of organoclay [79].

2.4 Characterization of Polymer Nanocomposites

Several different apparatus and techniques have been used to characterize polymer nanocomposites. These instruments include X-ray diffraction (XRD), transmission electronic microscopy (TEM), nuclear magnetic resonance (NMR), neutron scattering methods, and atomic force microscopy (AFM). Among these different techniques, the combinations of observations from XRD and TEM are well accepted as the best techniques to characterize polymer nanocomposites [13]. The basic theory of X-ray diffraction is explained here. The clay interlayer spacing can be calculated by Bragg's Law, $d_{001} = \lambda / 2 \sin \theta$, where λ is the wave length of X-ray (1.5418Å) [51]. The basal interlayer spacing of a layered silicate is estimated as 0.94 nm [15] and the corresponding reflection angle 2θ is 8.84°. Therefore, the general XRD scanning angle for polymer nanocomposites ranges from 0° ~ 10°. As polymer chains diffuse through and expand the clay gallery, the interspace between clay platelets increases. Therefore, the reflection angle 2θ decreases while the polymer chains get intercalated into the clay gallery. This change can be measured. X-ray diffraction is useful because it is quick and convenient, and it also provides a structural overview of the polymer nanocomposite tested.

Unfortunately, XRD can not always confirm the existence of an exfoliated structure. Sometimes the nanoclay particles are not even intercalated within the polymer matrix but a peak is not seen in the XRD pattern. This is because the clay platelets are randomly dispersed in the polymer matrix and the clay powder is disoriented. The signals being sent to the detector are weak. In addition, this is also related to the way XRD works at small diffraction angles [52]. Because of this, transmission electron microscopy becomes the

most useful technique to characterize polymer nanocomposites. TEM was first invented in 1934 by E Ruska, and the first TEM was manufactured by Siemens and Halske [53]. The resolving power of the first commercial TEM was 10 nm. Today, the resolving power of TEM could be as high as 0.14 nm. This high resolution makes TEM a powerful tool for characterizing nano sized materials. TEM can provide the detailed structure of polymer nanocomposites, but it can offer only localized information of a sample. Additionally, the sample preparation for TEM is time consuming. It usually takes 4 to 8 hours for a skillful technician to prepare one polymeric sample. Therefore, combining these two techniques, allows researchers to characterize polymer nanocomposites effectively. Morgan and Gilman did a comparative study of these two techniques for several different polymeric systems [52]. They ground the polymer nanocomposite pellets into powder or compression molded the pellets into a solid monolith and then did XRD analysis. They found that the XRD pattern was affected by the nature of the sample (powder or solid). This is well known in XRD analysis because the crystals that exist in the solids may have a preferred orientation, and this orientation may be removed when the samples are ground into powder. Therefore, XRD analysis is not always reliable in distinguishing exfoliated nanocomposites.

2.5 Mechanical Properties of Composites Materials

The mechanical properties of composite materials can be predicted by composite modeling equations such as the rule of mixtures [80, 81], the Hapin-Tsai Equation [82], or the Mori-Tanaka Equation [83]. These equations have been applied to conventional composites to predict the modulus of composite materials such as wood plastic composites

[81, 84]. In addition, these equations are applied to nanocomposites and found to be useful in recent years [15, 85 – 94].

The rule of mixtures is derived using a continuous fiber model [67]. If the applied stress is perpendicular to the fiber direction, the modulus of the composite can be written as:

$$\frac{1}{E_c} = \frac{V_m}{E_m} + \frac{V_f}{E_f} \dots\dots\dots (1)$$

On the other hand, if the applied stress is parallel to the fiber direction, the composite modulus can be written as:

$$E_c = E_m V_m + E_f V_f \dots\dots\dots (2)$$

Where:

E_c : Modulus of composites

E_f : Modulus of fiber

E_m : Modulus of matrix

V_f : Volume fraction of fiber in the composites

V_m : Volume fraction of matrix in the composites

Equations (1) and (2) are known as the upper bound and the lower bound of rule of mixtures.

Based on the micromechanical work derived by Hill [95, 96] and Hermans [97], Halpin and Tsai developed the well known Halpin-Tsai Equations to predict the modulus of unidirectional composites as a function of aspect ratio. Hill considered composites to be a single fiber encased in a cylinder of matrix with both embedded in an infinite medium. Hermans generalized Hill's self-consistent model to obtain an analytical solution in terms

of Hill's reduced modulus. Halpin and Tsai further reduced Hermans' results into a simpler analytical form which can be adapted for a variety of reinforcement geometries, including short discontinuous fillers [79, 98 – 100]. The general form of the Halpin-Tsai Equation is the following:

$$\frac{E}{E_m} = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} \dots\dots\dots (3)$$

Where ζ is the shape parameter which depends on filler geometry and loading direction, η is given by:

$$\eta = \frac{E_f / E_m - 1}{E_f / E_m + \zeta} \dots\dots\dots (4)$$

Halpin found that the Halpin-Tsai Equation fit the longitudinal modulus E_{11} well when $\zeta = 2(l / t)$. “l” and “t” represent length and thickness of the filler, respectively. The modulus perpendicular to the fiber direction (transverse modulus), E_{22} , is found to be less sensitive to the filler aspect ratio and can be approximated by $\zeta = 2$. It is worthwhile to note that when $l/d \rightarrow 0$, ($\zeta \rightarrow 0$), the Halpin-Tsai equation converges to the lower bound of rule of mixtures (Equation (1)). On the contrary, when $l/d \rightarrow \infty$, ($\zeta \rightarrow \infty$), the equation reduces to the upper bound of rule of mixtures (Equation (2)).

Another equation which has been widely utilized to predict the modulus of composite materials is the Mori-Tanaka Equation [83]. Mori and Tanaka derived an averaged stress theory based on Eshelby's inclusion model for determination of the elastic field of an ellipsoidal inclusion [101]. They further expanded Eshelby's model into a composite

containing many identical spherical particles. The internal stress in the composites is equal to the uniform average stress plus the local fluctuating stress from nearby inclusions. Tandon and Weng [102] utilized the Mori and Tanaka's assumptions and combined Eshelby's solution to derive analytical solutions for the elastic modulus of composites containing aligned sphere inclusions. Tandon and Weng's theory can predict the reinforcing effect of fibers, spheres and platelets by using either prolate or oblate spheroids [85]. Their results are written as follows:

(1) Longitudinal Young's Modulus E_{11} :

$$\frac{E_{11}}{E_m} = \frac{1}{1 + V_f (A_1 + 2v_m A_2) / A} \dots\dots\dots (5)$$

(2) Transverse Young's Modulus E_{22} :

$$\frac{E_{22}}{E_m} = \frac{2A}{2A + V_f [-2v_m A_3 + (1 - v_m) A_4 + (1 + v_m) A_5 A]} \dots\dots\dots (6)$$

In equations (5) and (6), v_m is the Poisson's ratio of the matrix and

$$\begin{aligned} A_1 &= D_1 (B_4 + B_5) - 2B_2 \\ A_2 &= (1 + D_1) B_2 - (B_4 + B_5) \\ A_3 &= B_1 - D_1 B_3 \\ A_4 &= (1 + D_1) B_1 - 2B_3 \\ A_5 &= (1 - D_1) / (B_4 - B_3) \\ A &= 2B_2 B_3 - B_1 (B_4 - B_5) \end{aligned}$$

where:

$$\begin{aligned}
B_1 &= V_f D_1 + D_2 + (1 - V_f)(D_1 S_{1111} + 2S_{2211}) \\
B_2 &= V_f + D_3 + (1 - V_f)(D_1 S_{1122} + S_{2222} + S_{2233}) \\
B_3 &= V_f + D_3 + (1 - V_f)[S_{1111} + (1 + D_1)S_{2211}] \\
B_4 &= V_f D_1 + D_2 + (1 - V_f)(S_{1122} + D_1 S_{2222} + S_{2233}) \\
B_5 &= V_f + D_3 + (1 - V_f)(S_{1122} + S_{2222} + D_1 S_{2233})
\end{aligned}$$

and

$$\begin{aligned}
D_1 &= 1 + 2(\mu_f - \mu_m)/(\lambda_f - \lambda_m) \\
D_2 &= (\lambda_m + 2\mu_m)/(\lambda_f - \lambda_m) \\
D_3 &= \lambda_m/(\lambda_f - \lambda_m)
\end{aligned}$$

λ_f , μ_f and λ_m , μ_m are the Lamé constants of the matrix and inclusions respectively.

$$\text{Where } \mu = \frac{E}{2(1 + \nu)} \text{ and } \lambda = \frac{\nu E}{(1 + \nu)(1 - 2\nu)} \quad [100]$$

For fiber like inclusions, the Eshelby tensors S_{ijkl} are given by:

$$\begin{aligned}
S_{1111} &= \frac{1}{2(1-\nu_m)} \left\{ 1 - 2\nu_m + \frac{3\alpha^2 - 1}{\alpha^2 - 1} - \left[1 - 2\nu_m + \frac{3\alpha^2}{\alpha^2 - 1} \right] g \right\} \\
S_{2222} = S_{3333} &= \frac{3}{8(1-\nu_m)} \frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4(1-\nu_m)} \left[1 - 2\nu_m - \frac{9}{4(\alpha^2 - 1)} \right] g \\
S_{2233} = S_{3322} &= \frac{1}{4(1-\nu_m)} \left\{ \frac{\alpha^2}{2(\alpha^2 - 1)} - \left[1 - 2\nu_m + \frac{3}{4(\alpha^2 - 1)} \right] g \right\} \\
S_{2211} = S_{3311} &= -\frac{1}{2(1-\nu_m)} \frac{\alpha^2}{\alpha^2 - 1} + \frac{1}{4(1-\nu_m)} \left\{ \frac{3\alpha^2}{\alpha^2 - 1} - (1 - 2\nu_m) \right\} g \\
S_{1122} = S_{1133} &= -\frac{1}{2(1-\nu_m)} \left[1 - 2\nu_m + \frac{1}{\alpha^2 - 1} \right] + \frac{1}{2(1-\nu_m)} \left[1 - 2\nu_m + \frac{3}{2(\alpha^2 - 1)} \right] g \\
S_{2323} = S_{3232} &= \frac{1}{4(1-\nu_m)} \left\{ \frac{\alpha^2}{2(\alpha^2 - 1)} + \left[1 - 2\nu_m - \frac{3}{4(\alpha^2 - 1)} \right] g \right\} \\
S_{1212} = S_{1313} &= \frac{1}{4(1-\nu_m)} \left\{ 1 - 2\nu_m - \frac{\alpha^2 + 1}{\alpha^2 - 1} - \frac{1}{2} \left[1 - 2\nu_m - \frac{3(\alpha^2 + 1)}{\alpha^2 - 1} \right] g \right\}
\end{aligned}$$

Where α is the aspect ratio of the inclusion ($= l / d$), and g is represented by:

$$g = \frac{\alpha}{(\alpha^2 - 1)^{2/3}} \left\{ \alpha(\alpha^2 - 1)^{1/2} - \cosh^{-1} \alpha \right\}$$

For a disk-shaped spherical inclusion, the expression of Eshelby's Tensors is similar to the case of fiber shape inclusions, but g is replaced with g' , where g' is given by:

$$g' = \frac{\alpha}{(1 - \alpha^2)^{2/3}} \left\{ \cos^{-1} \alpha - \alpha(1 - \alpha^2)^{1/2} \right\}$$

The disk-shaped spherical inclusion approach is especially useful for polymer-clay nanocomposites since the shape of layered silicate is similar to a spherical disk. Fornes et al provided a good literature review and experiments by applying the Halpin-Tsai Equation and the Mori-Tanaka Equation to predict the stiffness of polymer-clay nanocomposites.

The difference between fiber shape inclusions and sphere disk shape inclusions is given in Figure 2-14, and the important issues which limit the capability to model the mechanical properties of polymer nanocomposites are listed in Table 2-2 [15].

Figure 2-14 Physical representations of fiber and disk like reinforcement corresponding to the Halpin-Tsai and the Mori-Tanaka Equation [15]

Table 2-2 Some important issues that limit the ability to model the stiffness properties of polymer-layered silicate nanocomposites [15]

<u>Issue</u>	<u>Theory</u>	<u>Experimental</u>
Filler shape and size	<ul style="list-style-type: none"> - Uniform shape - Constant dimensions 	<ul style="list-style-type: none"> - Non-uniform shape - Distribution of lengths and thickness - Imperfect exfoliation of LAS
Filler orientation	<ul style="list-style-type: none"> - Unidirectional 	<ul style="list-style-type: none"> - Some degree of misalignment
Filler interface	<ul style="list-style-type: none"> - The filler and matrix are well bonded 	<ul style="list-style-type: none"> - Imperfect bonding between the filler and matrix
Filler modulus	<ul style="list-style-type: none"> - Assumes filler modulus is the same in all directions 	<ul style="list-style-type: none"> - Filler is anisotropic
Matrix considerations	<ul style="list-style-type: none"> - Assumes matrix is isotropic 	<ul style="list-style-type: none"> - Polymer chain orientation - Presence of polymer crystallites
Filler Concentration Effects	<ul style="list-style-type: none"> - No particle-particle interactions - Ignores changes in viscosity - No particle agglomeration 	<ul style="list-style-type: none"> - Particle-particle interactions and agglomeration - Changes in viscosity can alter morphology during injection molding - Changes in crystalline morphology (e.g. type, crystallite size, and amount)

Both the Halpin-Tsai Equation and the Mori-Tanaka equation have proved to be useful in the prediction of the stiffness of composite materials reinforced with macro-scale and nano-scale fillers. Although the Mori-Tanaka equation is more complicated but satisfying theoretically, the much simpler the Halpin-Tsai equations provide excellent predictions and

good approximations for engineers [104]. Finally, a good review paper written by Tucker and Liang reviewed several different theories of stiffness prediction of unidirectional short fiber composites including the equations mentioned in this section [105].

2.6 Foaming of Wood Plastic Composites

Although the bulk density of wood varies greatly between and within species, the value for most of species falls between 0.32 and 0.72 g/cm³ [106]. However, the true density of WF is around 1.4 g/cm³. When wood particulates are compounded with plastics, due to the high pressure generated by the extruder, the cellular structure of WF is either filled with plastics or collapsed by the high pressure. Therefore, the density of the WPCs would be much higher than those of wood. Foaming of WPCs is a good idea because it can reduce the density of WPCs and decrease the material cost. In addition, it also increases the nailing abilities of WPCs [107].

Foam can be defined as a denser continuum liquid or solid material containing gaseous voids. Generally, foaming can save 20 ~ 30wt% of material of plastics and thus make light weight products. In addition, the strength to weight ratio of foamed materials is significantly improved compared to unfoamed plastics [108]. In a foaming process, blowing agents are blended with plastics and gas is released during the extrusion process. Blowing agents can be classified in two categories. One is physical blowing agent (PBA) with the other one is chemical blowing agent (CBA).

Chemical blowing agents are chemicals which decompose and release gas at a certain temperature. Based on the reaction types, they are classified as (1) exothermic, (2) endothermic, and (3) exo / endothermic CBA. Exo / endothermic CBA is considered to be

a mixture of exothermic CBA and endothermic CBA. Some typical chemical reactions of CBA are given by the following [33]:

Exothermic Reaction:

Endothermic Reaction:

And plastics are foamed after the gas releases. Chemical blowing agents are applied in the foaming industry due to their low cost. However, it is not easy to control the cell size during the extrusion and a batch to batch difference of CBAs can result in cell structure differences. The requirements of the ideal CBA are listed as follows [38]:

- (1) Decomposition reaction has to be in a defined temperature range, according to the polymer used.
- (2) Avoid very fast reaction (explosion) by decomposition of the CFA.
- (3) Prevention of a heat build-up or burning.
- (4) Easy mixing and uniform dispersion of the CFA in the polymer.
- (5) High gas yield and feasibility of the CFA.
- (6) CBA should not be corrosive for tools.
- (7) No discoloration and plate out of the polymer.

Here, plate out means fillers are floating on the surface of polymer instead of entering the formulation during processing. Thus, fillers can be seen on the surface of samples.

Physical blowing agents were developed in the 1980s. Professor N. P. Suh at MIT developed a new process by dissolving carbon dioxide into polymers in a high pressure vessel. After a certain time, the polymers were saturated with gas. Then the pressure was quickly released to cause thermodynamic instability, and gas was evolved from polymers. By properly controlling the pressure and temperature, foamed plastics were obtained [109 – 111]. Later on, the batch foaming process was developed and facilitated in the extrusion and injection molding processes. By this method a cell size is more uniform and “microcellular foam” can be obtained. The microcellular foams are characterized by a cell size less than $10\mu\text{m}$ and cell density larger than 10^9 cells/cm³ [112]. Typical microcellular plastic foams exhibit high impact strength or toughness and high fatigue life [113]. Carbon dioxide is the preferred physical blowing agent in a microcellular foaming process because of its unique properties. These properties are (1) the solubility of CO₂ in polymer melts at elevated pressure is high [114, 115] and (2) the diffusivity of CO₂ in polymer is large, which guarantees a fast mixing process [112]. When carbon dioxide is heated and pressurized beyond its critical temperature (304.1K) and pressure (7.38MPa), it is called supercritical carbon dioxide (SC-CO₂) [116]. When CO₂ reaches its supercritical state, it possesses both the properties of liquid and gas. It diffuses through polymer melts quickly and forms a single phase liquid during the mixing process. Therefore, CO₂ at supercritical state is a more favorable physical blowing agent. Nitrogen is a good candidate for PBA, too, because it is cheap, inert, and the critical point is similar to CO₂. However, it is not easy to

foam plastics with N₂ since the solubility of supercritical N₂ in the polymer melts is much lower than that of CO₂ [117].

Foaming with physical blowing agents has been an active research area in academic institutes since the cell structure and cell densities are better controlled. Nevertheless, the plastic industry is somehow reluctant to foam plastics using PBA due to the high equipment cost. On the other hand, the research and development work done by CBA suppliers makes it possible to obtain a microcellular foam using CBA.

In the past, both of PBA and CBA had been used to foam wood plastic composites using batch, extrusion or an injection molding process. Lots of the research has been done by Park and coworkers, (extrusion) [20, 77, 79, 118 – 124], Bledzki et al. (extrusion, injection molding) [28, 33 – 38], and Matuana et al. (batch and extrusion) [125 – 139]. The base polymers which have been applied in WPCs foaming are HDPE, PP, PVC and PS. Due to the limited availability of equipment, very few papers have been published using extrusion foaming with PBA [120, 124, 140] while the other works were done by batch foaming.

Park et al. developed a tandem extrusion system which connects one twin screw extruder and one single screw extruder in series to foam HDPE-based pine wood WPCs (Figure 2-15). A vent port was installed at the junction of two extruders to take off water vapor and volatile organic compounds released from the WF. The quality of HDPE-WPCs foams was characterized by measuring the expansion ratio of the WPCs foamed by a single screw extruder and a tandem extrusion system. WPCs foamed with the tandem extrusion system showed better expansion ratio and better cell structure. From their observation, water is detrimental for foaming of WPCs. This is because water has very low solubility in

polymer and water vapor will condense into liquid after the pressure drops. These characteristics of water vapor make it hard to get a uniform cell size distribution in the WPCs.

Figure 2-15 Tandem Extrusion System developed by Park et al. [118]

Other than moisture, WF has volatile compounds that can interfere with the foaming process. Park et al. characterized volatile emissions from pine WF at different temperatures by TGA [20]. First, the pine WF was dried at various designated temperatures for 12 hrs and extracted with acetone for 6 hrs. It was found that un-dried WF contained 10wt% of extractives and 4 ~ 5wt% of the extractives were evaporated during the compounding process. In addition, the higher the heating rate was, the less the volatile compounds that were evolved. The isothermal TGA thermograph was pre-dried and had the effect of moisture eliminated is shown in Figure 2-16. It was found that WF releases much more gas when the temperature is above 175°C. It is of interest to investigate the effect of volatile

compounds in the foaming of WPCs. Park et al. found that by foaming WPCs with the volatile compounds, the density of WPCs can be as low as 800kg/m^3 [119]. However, since the cell structure of WPCs foamed with volatile compounds was not easily controlled, it is undesirable to generate volatile compounds from WF during processing.

Figure 2-16 Isothermal thermograph of un-dried WF at high temperatures.

In summary, Park et al. provide some suggestions for the foaming of WPCs using a tandem extrusion system [122]:

- (1) To minimize the foaming effects of volatiles generated from WF, the highest foaming processing temperature should be below 170°C
- (2) The longer the residence time in the 1st extruder, the more the volatile emissions of WF in the 2nd extruder are decreased
- (3) The lower the residence time in the 2nd extruder, the lesser are the emissions from the WF.
- (4) Dr. Park suggests using a process temperature as low as possible, preferably below 160°C

After finding the optimized conditions of foaming, Park et al. foamed WPCs using CBA [121] and CO₂ [120], respectively. By properly controlling the die temperature of the 2nd extruder, the density of foamed WPCs could be as low as 300 ~ 400kg/m³. Additionally, it was found that coupling agent is helpful in the foaming of WPCs.

Bledzki and Faruk foamed PP-based WPCs with exothermic, endothermic and exo endothermic chemical blowing agents, mainly in injection molding. The other variables which have been discussed are loading level of CBA, viscosity of base polymer, wood content, mold filling rate and mold temperature. The quality of the foams was not only characterized by microscopic pictures, but also by mechanical properties, rate of water absorption and surface roughness. The density of PP-WPCs foams can be reduced to 700kg/m³ by injection molding foaming. In summary, they found that exothermic type CBA is the most effective CBA while endothermic type CBA provided the best surface quality. Higher mold temperatures and higher filling rates are preferred in WPC injection molding foaming. Since WF can not be foamed, the density of WPCs increases with the wood content. High melt flow index PP (low viscosity) provides better foam structure for PP-based WPCs.

2.7 Summary

In summary, the objective of this work is to develop a high strength, high modulus and light weight wood plastic composite and thus make WPCs into structural material. Nanofillers such as nanoclay are considered to be one of the good candidates to increase the modulus of PP-based WPCs. By properly controlling the processing conditions, nanoclay can be exfoliated in wood plastic composites. The theoretical modulus of wood

plastic composites can be predicted by composite modeling equations such as the Mori-Tanaka equation and the Halpin-Tsai equation. The ductility of WPCs may be improved by adding elastomers. By adding additives such as a coupling agent, UV stabilizer and lubricant and fungicide, the properties of WPCs can be improved and their applications can be expanded.

CHAPTER 3 MATERIALS AND EXPERIMENTS

3.1 Materials Used

In all of the experiments, the following materials have been used:

Wood flour: Maple wood flour of 80-mesh size (about 177 μm) was provided by American Wood Fiber (Maple 8010). According to manufacturer 60% of WF passed 120 mesh sieves (125 μm) The moisture of WF was determined by ASTM D4442 to be 5 ~ 6wt%. WF was pre-dried in the oven at 100°C for 7 hours to ensure that the moisture content is less than 1wt%.

Polypropylene: BP Amoco's polypropylene homopolymer PP1246 (melt flow index = 20g / 10min at 230°C and 2.16kg, ASTM D1238).

Two kinds of clay were used in the experiments: NanoblendTM1001 master batch and Nanomer[®] I.30P nanoclay powder.

NanoblendTM1001: Pre-compounded PP/clay master batch pellets containing 38~42wt% of coated clay and gifted by PolyOne. The detailed composition of PP/clay master batch was not available from the manufacturer. The NanoblendTM master batch was only used in the work described in Chapter 4 and Chapter 5.

Nanomer[®] I.30P: an organoclay powder purchased from Nanocor. The organoclay powder I.30P was octadecylamine-modified montmorillonite clay of initial d basal spacing of 2.3nm [68]. The organoclay powder was pre-dried in the oven at 85°C for 12 hours to remove moisture.

PP-g-MA compatibilizer: PolyBond[®] 3200 from Crompton (now Chemtura); it has a molecular weight of 120,000 (g/mol) with 1.0wt% MA content. The melt flow index of PolyBond[®] 3200 is 115 g/10min at 2.16kg load and 190°C.

Antioxidant: Naugard[®] B-25 was also provided by Crompton (now Chemtura); it is a blend of tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]metha and tris-(2, 4-di-t-butylphenyl)phosphate in 1:1 ratio, and it is used to prevent polymer degradation during melt compounding.

3.2 Compounding

3.2.1 Screw Design

WPCs were compounded using a Leistritz Micro-27 twin screw extruder (L/D = 40, D=27mm), and this extruder can be operated with both co-rotation and counter rotation screws. All the samples were compounded using co-rotation screws unless specifically mentioned otherwise. The screw design charts of co-rotation screws and counter rotation screws are shown in Figures 3-1 and 3-2, respectively.

Figure 3-1 Screw geometry of co-rotation screws. L:D = 40:1

Figure 3-2 Screw geometry of counter-rotation screws. L:D = 40:1

The processing temperature of WPCs was kept below 200°C. This was to prevent the WF from degrading; therefore, the temperature in the extruder increased from 165 to 180°C.

3.2.2 Processing parameters

3.2.2.1 Two Step Compounding

The PP-layered silicate master batch, Nanoblend™ 1001, was first diluted with PP to get PNCs containing 2wt%, 4wt%, and 10wt% of layered silicate using the Leistritz Micro-27 co-rotating twin screw extruder. The pellets of both the polymer and the master batch were hand mixed and fed to the extruder using a K-Tron loss-in-weight feeder at a total feeding rate of 5kg/hr. The temperature was set at 185 °C at the hopper, and it was increased to 210°C at the die. The PNC strands were extruded into a water bath and then pelletized.

Once the extruder operating conditions were fixed, the WF was compounded with the previously-made PNC pellets to get WPC samples containing different loading levels of clay in the matrix. In this process, the amount of the PP-g-MA coupling agent was varied so that the amount of coupling agent in the WPCs was 0%, 2%, 4% or 10% of the weight of WF in the WPC. In each formulation, the antioxidant was added at a level of 0.1wt% of the total WPC. In this manner, WPCs containing of WF and clay and PP-g-MA were prepared. The weight of each batch was 2kg.

3.2.2.2 One Step Compounding

Materials were fed into the twin screw extruder using K-Tron SODER K-CL-24-KQx4 pellet feeder and K-CL-24-KT20 powder feeder, respectively. Both of the feeders were controlled by a KSL Smart Line Control Display. PP and PP-g-MA pellets were hand mixed in a bag and fed in to the pellet feeder. Again, powder materials such as WF, antioxidant, and/or nanoclay were hand mixed in a bag and fed into powder feeder. In

these experiments, materials are all added together into the hopper of the twin-screw extruder at the same time. The processing variables were controlled at either 2.4kg/hour at screw speed of 85rpm or 4.8kg/hr at screw speed of 150rpm unless specified otherwise for wood plastic composites.

3.2.3 Injection Molding

The compounded pellets were pelletized and dried in an oven at 85°C for 5 hours before injection molding. The compounded PNC or WPC pellets were dried at 85°C for 5 hours and then injection molded using a Battenfeld BA 1000-CDC injection molding machine to produce standard ASTM samples. The barrel temperature was controlled between 165 ~ 175°C. The injection pressure was fixed at 68.95MPa (10000 psi) while the holding pressure was fixed at 27.58MPa (4000 psi).

3.2.4 Mechanical Testing and Other Analyses

The tensile and flexural strength and stiffness properties of these specimens were measured using an Instron 5567 universal testing machine. The tensile and flexural tests refer to ASTM D638 and D790 respectively. The cross sectional area of tensile sample is 13mm x 3.2mm while the overall length of the samples is 165mm (ASTM D638, Type I). The tensile and flexural test samples were tested with a cross head speed of 5mm/min and 1.27 mm/min, respectively. The modulus and strength of the samples were determined when the standard deviation is less than 15% of the average. At least five samples were tested from each batch.

Because WPCs generally showed relatively low impact strength in the standard Izod impact tests, the reversed notch impact test method was applied using an Instron/Satec

impact testing machine model BLI (ASTM D256). Due to the high standard deviation of the impact strength of composites, the impact strength was determined when the standard deviation is less than 30% of the average. At least five samples were tested from each batch.

The impact and tensile fracture surfaces of the WPCs obtained from mechanical testing were sputter coated with gold and examined with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM).

The extent of clay dispersion in the PP-organoclay nanocomposites was determined with the help of transmission electron microscopy. The TEM pictures shown in Chapters 4 and 5 were carried out at Tulane University in New Orleans, LA. On the other hand, the TEM pictures shown in Chapter 7 were taken using a JOEL 100 CX TEM with (cryo-ultramicrotome) at West Virginia University.

The density of injection molded samples was determined by a Micromeritics AccuPyc 1330 helium pycnometer. In this way, the true density of WF and organoclay were determined.

The rate of water absorption of the WPCs was determined using a “blot and weigh” method. Three weighed samples were taken from each batch to conduct this test. The typical injection-molded impact test sample of 12.5mm x 64mm x 3.175mm was put on a tray of desiccants and dried in a vacuum oven at 80°C for 12 hours. After that, each sample was soaked in a sealed container full of distilled water at room temperature and was periodically removed and weighed. The results of the water absorption test were plotted as percentage weight gained versus time of immersion. These samples are considered to have reached the equilibrium moisture when the weight gain was less than 3mg within a two week period.

CHAPTER 4: INCREASING MODULUS OF PP-BASED WPCS BY ADDING NANOCLAY

4.1 Introduction

This chapter is based on our paper published in Journal of Polymer Engineering in the December 2006 issue. The modulus of PP-based WPCs is increased by adding nanoclay in the WPCs.

4.2 Objectives

In this study, improving the mechanical properties of WPCs will be the major issue to be discussed. The reason is that the flexural modulus of solid wood is around 9GPa, while the corresponding value of PP is only slightly more than 1GPa [8]. Therefore, any combination of WF and plastic will lead to WPC flexural and tensile moduli that are significantly lower than those of natural wood. A deck constructed out of WPC, therefore, will flex much more than an identical wood deck for the same load. This is undesirable, and the problem can be solved either by increasing the wood content of WPCs or by improving the mechanical properties of the matrix polymer. The first method would appear to be more straightforward; however, increasing the wood content of WPCs above 50wt% leads to processing problems during strand extrusion – unacceptably high extruder torque and melt fracture, for example. Also, at a still higher wood content, there is the possibility that the wood particulates may not be properly encapsulated by the polymer. Thus, it may happen that the amount of moisture uptake by the WPC on exposure to the environment may increase. Therefore, the concept of increasing the modulus of the matrix is quite attractive. There are at least two avenues available to increase the modulus of the polymer

matrix: one is to use stiffer polymers such as acrylonitrile-butadiene-styrene (ABS) while the other one is to add nanofillers such as layered silicates, i.e. to employ polymer nanocomposites (PNCs) as the matrix material. Here the latter approach is of more interest since it is possible to double the modulus of polyolefins by the incorporation of only a few wt% of well-dispersed nanoclay. Additional advantages of PNCs as matrix materials are the likely improvement in barrier and flammability properties as compared to the neat polymer [140]. Because it is possible to use a twin-screw extruder for both compounding and profile extrusion, a twin-screw extruder was used in the experiment for compounding and pelletizing; the pellets can then be fed to a single-screw extruder for profile extrusion or to an injection molding machine to make moldings.

Although enhancing the modulus of WPCs is important, the possibility of developing low strength due to improper extrusion-compounding is another concern. Since polyolefins are non-polar (hydrophobic) materials while wood particulates are polar (hydrophilic) materials, there is a high probability of obtaining poor adhesion between wood and polymer; this results in low tensile and flexural strengths of the WPCs [6]. In order to improve the adhesion between wood and plastics, PP-g-MA is generally introduced as a coupling agent. On the other hand, PP-g-MA also acts as a dispersant and compatibilizer to enhance the melt intercalation of PP molecules into the galleries of clay platelets. Therefore, it is of interest to study the effect of loading level of the coupling agent on the properties of WPCs formulated employing PP/clay nanocomposites as the matrix. In addition, results are likely to be influenced by the mixing procedure and the chosen process conditions.

In terms of explaining the results, the rule of mixtures is a common equation utilized to predict the modulus of continuous fiber reinforced composites. It can be

modified with the help of correction factors, and the resulting modified rule of mixtures can be applied to polymers reinforced with discontinuous fibers. This modified rule of mixture is applied here to explain the modulus of WPCs formulated with different loading levels of layered silicates.

4.3 Experimental Details

4.3.1 Sample Preparation

4.3.2.1 Two-Step Compounding Employing PP/clay Master Batch

The detailed compounding procedure of a two step compounding process is mentioned in section 3.2.2. The PP-layered silicate master batch, Nanoblend™ 1001, was first diluted with PP to get PNCs containing 2wt%, 4wt%, and 10wt% of layered silicate using a twin screw extruder and co-rotation screws. Since the clay content of the master batch is around 38 ~ 42wt% and the density of the Nanoblend™ master batch and PP are known, the density of coated clay can be calculated as 1410kg/m³. In view of this, the volume percentage of clay in the matrix for the clay contents of 2wt%, 4wt% and 10wt% are estimated to be 1.4vol%, 2.75vol%, and 7vol% respectively.

Wood plastic composites having 50wt% of WF were subsequently prepared using the same twin-screw extruder. The detailed compounding procedure can be found in section 3.2.2.1 as well.

A series of scouting runs of WPCs without nanoclay was conducted on the Leistritz extruder to establish optimized operating conditions, and the results are listed in Table 4-1; in this table, the quantity called SME is the calculated specific mechanical energy, and it is defined fully later in the chapter. In these experiments, the amount of PP-g-MA

added was fixed at 4wt% of WF. Based on this work, and in order to get the highest strength, a low screw speed of 85rpm and a low total feeding rate of 2.4kg/hr were chosen for the WPC compounding process. Detailed information of processing variables versus the mechanical properties of WPCs will be discussed later.

Table 4-1 Effect of compounding conditions on the mechanical properties of WPCs containing 50wt% WF

Total Feeding Rate (kg/hr)	Torque (%)	Screw Speed (rpm)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Failure Strain (%)	Flexural Modulus (GPa)	Flexural Strength (MPa)	SME (J/g)
2.4	33	85	4.26 ± 0.13	39.8 ± 0.2	3.41 ± 0.1	3.67 ± 0.03	67.89 ± 0.26	441
4.8	51	85	4.22 ± 0.19	37.08 ± 0.47	2.83 ± 0.13	3.49 ± 0.04	61.11 ± 0.39	340
8	78	85	3.91 ± 0.11	34.06 ± 0.67	2.78 ± 0.16	3.4 ± 0.04	57.11 ± 0.47	312
2.4	30	150	4.59 ± 0.16	35.68 ± 0.38	2.17 ± 0.14	3.68 ± 0.07	58.71 ± 0.53	707
4.8	40	150	4.22 ± 0.17	36.52 ± 0.12	2.49 ± 0.05	3.48 ± 0.01	59.88 ± 0.35	471
8	55	150	4.1 ± 0.08	33.66 ± 0.22	2.45 ± 0.08	3.45 ± 0.03	55.79 ± 0.37	389
4.8	40	300	4.4 ± 0.19	37.04 ± 0.11	2.64 ± 0.08	3.62 ± 0.02	60.3 ± 0.16	942
8	45	300	4.4 ± 0.16	34.85 ± 0.29	2.5 ± 0.07	3.55 ± 0.03	56.83 ± 0.53	636
16	68	300	4.03 ± 0.09	32.41 ± 0.11	2.44 ± 0.14	3.41 ± 0.01	54.19 ± 0.67	481

Once the extruder operating conditions were fixed, the WF was compounded with the previously-made PNC pellets to get WPC samples containing different loading levels of clay in the matrix. In this process, the amount of the PP-g-MA coupling agent was varied so that the amount of coupling agent in the WPCs was 0%, 2%, 4% or 10% of the weight of WF in the WPC. In each formulation, the antioxidant was added at a level of 0.1wt% of the total WPC. In this manner, sixteen different batches of WPCs containing 50wt% of WF and different amounts of clay and PP-g-MA were prepared. The weight of each batch was 2kg. In addition, another three batches of WPC samples were compounded with 55wt%, 60wt%, and 65wt% of wood content respectively to compare the effect of using clay at the 50wt% wood level to the effect of increasing the wood content alone on the modulus of

elasticity of WPCs. The loading level of PP-g-MA in these three samples was kept fixed at 4% of the weight of WF. Finally, some WPC samples having 50wt% wood and 20wt% clay in the matrix were also prepared.

4.3.2.2 One Step Compounding Using Organoclay

Instead of using the PNC master batch, Nanomer[®] I.30P organoclay powder was used in the compounding process. The detailed compounding procedure can be found in section 3.2.2.2. This had the added advantage that it allowed for a more precise estimate of the actual clay content in the WPCs. The product was compounded WPCs containing 2, 4, and 10wt% of layered silicate in the polymer matrix. Note that now PP-g-MA not only acts as coupling agent between wood and PP but also as a compatibilizer between clay and PP. Therefore, the amount of PP-g-MA in these experiments was a sum of two quantities: 4wt% of WF plus 3 times the weight of nanoclay [63, 68]. Two different compounding conditions were adopted in these experiments. Each formulation of WPCs was compounded at 85rpm and 2.4kg/hr and also at 150rpm and 4.8kg/hr to investigate the effect of compounding process conditions on the mechanical properties of WPCs.

Since the molecular weight of the PP-g-MA is different from that of PP, three batches of PP/PP-g-MA samples were compounded to understand the potential effect that a high concentration of PP-g-MA in the matrix might have on the mechanical properties. Additionally, three batches of PP-layered silicate samples containing 2, 4 and 10wt% of layered silicate were prepared by compounding Nanomer[®] I.30P with PP to obtain the mechanical properties of the PNC that forms the matrix of the WPCs. The amount of PP-g-MA in these three batches was 3 times the weight of nanoclay.

4.4 Results and Discussion

4.4.1 Two-Step Compounding

A TEM picture of the nanocomposite containing 10wt% organoclay, and obtained by diluting the PP/clay master batch, is shown in Figure 4-1. It is seen that the clay platelets are not exfoliated; rather, they are intercalated with PP. Nonetheless, the mechanical properties of the PNC samples, and these are presented in Table 4-2, are significantly improved. As is evident, both the tensile and flexural modulus increase with the loading level of layered silicate and these increases are statistically significant. The values of F test of the tensile and flexural moduli are 117.83 and 4592.84, respectively, and both these values are much larger than $F_{0.05,4,20} = 2.866$. (See Table A1-1(a) and A1-1(b) in Appendix I). Even as the modulus values more than double, the flexural strength is enhanced while the tensile strength remains unchanged in the presence of clay.

Figure 4-1 TEM picture of a PNC sample containing 10wt% clay (100000x)

Table 4-2 Mechanical properties of PNCs prepared by diluting the Nanoblend™ 1001 master batch

Clay Content (wt%)	Organoclay Content, vol% (Estimated)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Density (kg/m ³)
0	0	1.26 ± 0.02	29.59 ± 0.09	1.07 ± 0.02	35.11 ± 0.11	911.8
2	1.43	1.41 ± 0.13	28.02 ± 0.12	1.36 ± 0.03	39.89 ± 0.46	917.9
4	2.75	1.53 ± 0.06	30.04 ± 0.35	1.62 ± 0.01	43.51 ± 0.09	930.8
10	7	1.96 ± 0.07	31.47 ± 0.36	2.06 ± 0.01	47.42 ± 0.1	947.1
20	14.57	2.65 ± 0.18	30.70 ± 0.55	2.72 ± 0.06	50.26 ± 0.19	982.6

The results of the tensile and flexural moduli of the WPCs containing different amounts of clay and PP-g-MA are shown in Figures 4-2 and 4-3, respectively. It is seen that the moduli of WPCs increase with an increase in clay loading level, especially at a PP-g-MA loading level of 4wt%. It is interesting to point out that at a PP-g-MA loading level of 4wt%, WPCs possesses higher modulus than other samples of the same clay loading level. The reason for this has to be further investigated. At this PP-g-MA content, the flexural modulus of WPCs containing 50wt% wood and 4wt% nanoclay in the matrix is equal to the flexural modulus of WPCs containing 60wt% wood (see Table 4-3). Simultaneously, the tensile modulus of WPCs containing 50wt% wood and 10wt% clay in the matrix equals the tensile modulus of WPCs containing 60wt% wood but no clay. It should be reemphasized, though, that it is ordinarily difficult to process PP-based WPCs with more than 55wt% WF. This is because the extruded strands become very brittle and are not easy to pelletize. Based on the results presented in this section, it would appear to be more practical to incorporate nanoclay in the polymer matrix to improve the modulus of WPCs instead of increasing the wood content.

Table 4-3 Mechanical properties of WPCs containing different levels of wood with 4 wt% PP-g-MA

Wood Content wt%	Tensile Modulus GPa	Tensile Strength MPa	Flexural Modulus GPa	Flexural Strength MPa
50%	4.26 ± 0.13	39.8 ± 0.2	3.67 ± 0.03	67.89 ± 0.26
55%	4.5 ± 0.06	36.61 ± 0.16	3.72 ± 0.01	62.18 ± 0.05
60%	4.73 ± 0.19	38.01 ± 0.37	4.03 ± 0.02	64.09 ± 0.5
65%	5.26 ± 0.25	38.34 ± 0.39	4.39 ± 0.03	64.33 ± 0.31

Figure 4-2 Tensile modulus of WPCs containing 50wt% wood and different amounts of clay and PP-g-MA

Figure 4-3 Flexural modulus of WPCs containing 50wt% wood and different amounts of clay and PP-g-MA

As expected, at a given clay content, the tensile and flexural strengths of the WPCs increased with increasing amounts of coupling agent, sometimes by as much as 100%, and these results are displayed in Figures 4-4 and 4-5, respectively. As can be seen in the first column of Figures 4-4 and 4-5, at 0wt% clay the strengths of WPCs increase with the loading level of PP-g-MA. The tensile strength of WPCs increases from 22MPa to 40MPa while the loading level of PP-g-MA increases from 0% to 4wt%. More coupling agent does not provide too much strength to WPCs. For example, the tensile strength increased only by 3MPa when the loading level of PP-g-MA increased from 4wt% to 10wt% as can be seen in Figure 4-4. As previously mentioned, at a given clay content, WPCs shows higher modulus at 4wt% of PP-g-MA. Therefore, adding 4wt% of PP-g-MA to wood in the WPCs seems to be the optimized loading level for this system.

Figure 4-4 Tensile strength of WPCs containing 50wt% wood and different amounts of clay and PP-g-MA

Figure 4-5 Flexural strength of WPCs containing 50wt% wood and different amounts of clay and PP-g-MA

The absolute strength value depends on the amount of clay in the matrix; the higher the clay content, the smaller is the strength. This was unexpected since the loading level of PP-g-MA was kept proportional to the wood content. Thus, while the modulus of the PNC-

based WPCs increases with amount of added clay, the tensile and flexural strengths decrease. These data suggest that the affinity between WF and the polymer matrix was negatively affected in the presence of clay. The explanation for this reduction in strength becomes clear upon examining the SEM micrographs of the fracture surfaces of WPCs. As can be seen in Figure 4-6, for a WPC sample containing 4wt% PP-g-MA, there are many broken wood fibers embedded in the fracture surface than there are fibers that have been pulled out. This means that the wood fiber bonds well to the neat PP. On the other hand, WPC samples of the same composition, but made with a PNC containing 4wt% clay in the matrix, showed significantly more fiber pull out as evidenced by holes on the fracture surface; these can be seen in Figure 4-7. These two pictures provide graphic evidence that the reduction in strength of WPCs in the presence of clay in the PP is the result of poor adhesion between the wood and the PNCs.

Figure 4-6 Fracture surface of WPC sample containing 50wt% wood and 4wt% of PP-g-MA

Figure 4-7 Fracture surface of WPC sample containing 50wt% wood and 4 wt% of PP-g-MA. Now the matrix also has 4wt% clay.

In closing this section, it has been noticed that while the observed trends with varying wood content, coupling agent content and clay content are independent of the extruder operating conditions, the absolute values of the observed mechanical properties are not. This is not surprising. Since a twin-screw extruder is typically starve-fed, the screw speed and extruder throughput are both independent variables. They determine the residence time in the extruder, and this can influence the extent of a chemical reaction. They also influence the energy put into the material, and this can affect the mixing intensity and, consequently, the extent of filler dispersion. Thus, while it is always desirable to increase the production rate, a proper balance has to be achieved between screw rotation rate and the mass flow rate in order to obtain desired mechanical properties. In this regard, it is customary to calculate the specific mechanical energy (SME) which is defined as [141]:

$$SME(J / g) = \frac{Screw\ Speed(N) \times (\%Torque) \times gear\ box\ rating(N \cdot m)}{955000 \times total\ feeding\ rate(kg / hr) \times \frac{1000}{3600}} \times 1000 \dots (10)$$

SME has units of energy/mass, and calculated values of this quantity are also listed in Table 4-1. Tensile properties of WPCs listed in this table are sketched as a function of the SME in Figures 4-8 and 4-9; the results of flexural properties are very similar. As can be seen from these figures, both strength and stiffness improve with decreasing screw speed when the SME value is kept fixed; this is a residence time effect, and it probably influences the reaction between the maleic anhydride and the wood particulates. Again, mechanical properties improve with increasing SME at a fixed screw speed. This is a result of better mixing and filler dispersion. There are a couple of points in Figures 4-8 and 4-9 that do not appear to follow these general trends. This is because, at those processing conditions, the melt temperature went up, and the wood fibers began to degrade. Also, under some conditions, strength and modulus could be lowered by fiber attrition, but the truth of this hypothesis has not been verified.

Figure 4-8 Tensile modulus of WPCs as a function of the specific mechanical energy. WPC contains 50wt% WF and 4wt% PP-g-MA to WF

Figure 4-9 Tensile strength of WPCs as a function of the specific mechanical energy. WPC contains 50wt% WF and 4wt% PP-g-MA to WF

4.4.2 One Step Compounding

As the amount of clay in the WPC increases during one-step compounding, the matrix becomes richer in PP-g-MA at the expense of PP. Since the molecular weight of PP-g-MA is usually lower than that of PP, this is likely to influence the properties of the WPC, especially when the loading level of clay is 10wt%. To determine if this might happen, three different batches of mixtures of PP and PP-g-MA were compounded under two different extrusion conditions, and the resulting mechanical properties were measured; these are reported in Table 4-4. Though the change in tensile modulus is statistically significant, a 0.1GPa difference in tensile modulus is very common for plastics (See Appendix I, Table 1-2(a) to 1-2(d)). Also, the differences in flexural modulus of these samples are statistically insignificant. Fortunately, the mechanical properties of the PP/PP-g-MA blends show only slight changes with increasing percentages of PP-g-MA.

Table 4-4 Mechanical properties of mixtures of PP and PP-g-MA

PP-g-MA Content (wt%)	Tensile Strength (MPa)	Tensile modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)
2.4kg/hr 85rpm				
0%	29.59 ± 0.09	1.26 ± 0.02	35.11 ± 0.11	1.07 ± 0.02
10%	26.31 ± 0.16	1.34 ± 0.04	34.05 ± 0.89	1.08 ± 0.03
17%	25.96 ± 0.13	1.34 ± 0.07	33.64 ± 0.09	1.06 ± 0.02
38%	26.02 ± 0.05	1.40 ± 0.07	33.91 ± 1.56	1.07 ± 0.06
100%	24.93 ± 0.17	1.37 ± 0.02	35.16 ± 0.59	1.04 ± 0.03
4.8kg/hr 150rpm				
0%	29.59 ± 0.09	1.26 ± 0.02	35.11 ± 0.11	1.07 ± 0.02
10%	25.98 ± 0.31	1.33 ± 0.03	33.46 ± 0.12	1.04 ± 0.01
17%	25.80 ± 0.07	1.32 ± 0.03	33.34 ± 0.10	1.05 ± 0.01
38%	26.10 ± 0.09	1.37 ± 0.06	35.01 ± 0.41	1.08 ± 0.02
100%	24.93 ± 0.17	1.37 ± 0.02	35.16 ± 0.59	1.04 ± 0.03

The properties of PNCs formulated with the Nanomer[®] I.30P organoclay and appropriate amounts of PP and PP-g-MA are listed in Table 4-5. If these data are compared to those shown earlier in Table 4-2, it can be found that the mechanical properties of PNCs made with Nanomer[®] I.30P and PP-g-MA appear not to be as good as those of PNCs made using the Nanoblend[™] 1001 master batch. However, as Figure 4-10 reveals, the WPCs made with Nanomer[®] I.30P plus 3 times of PP-g-MA actually showed better mechanical properties than those made with Nanoblend[™] 1001. In addition, the density of PNCs made by diluting the master batch with PP is different from that made by compounding clay powder with PP. This might be because the Nanoblend[™] 1001 master batch probably contains some other chemicals that might interact with the reaction of PP-g-MA with wood.

Figure 4-10 Comparison of mechanical properties of WPCs made with one-step and two-step compounding processes. In the latter case, two different process conditions are employed.

WPC mechanical properties resulting from the one-step compounding process employing two different processing conditions are shown in Figure 4-10. As can be seen from this figure, the mechanical properties of WPCs produced with this process are superior to those of WPCs made with the two-step process. Moreover, there is little difference in the mechanical properties of the WPCs made at 2.4kg/hr and 85rpm versus those made at 4.8kg/hr and 150rpm. According to Table 4-1, the SME values in the two cases are comparable, and the results are consistent with those shown in Figures 4-8 and 4-9 (where there was no clay present). One would clearly prefer the higher mass flow rate.

Table 4-5. Mechanical properties of PP-based nanocomposites with different amounts of Nanomer® I.30P

Clay Content (wt%)	Clay Content vol% (Estimated)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Density (kg/m ³)
0	0	1.26 ± 0.02	29.59 ± 0.09	1.07 ± 0.02	35.11 ± 0.11	911.8
2	1.43	1.37 ± 0.04	26.71 ± 0.22	1.11 ± 0.01	33.15 ± 0.12	910.4
4	2.75	1.45 ± 0.04	26.5 ± 0.15	1.19 ± 0.02	34.88 ± 0.19	919.8
10	7.00	1.81 ± 0.02	25.87 ± 0.07	1.41 ± 0.05	37.31 ± 0.91	948.8

To determine if the improvement in WPC mechanical properties obtained as part of this research was what might reasonably be expected, the rule of mixtures was used for guidance. According to this rule, the modulus of a continuous-fiber-reinforced composite is:

$$E_c = E_m V_m + E_f V_f \dots\dots\dots (2)$$

where E_c , E_f and E_m are the moduli of the composite, fiber and matrix, respectively, and V_f is the volume fraction of fibers. For the situation at hand, equation (2) can be modified by including a length correction factor η_L and an orientation correction factor η_o as shown below:

$$E_c = E_f \eta_L \eta_o V_f + E_m (1 - V_f) \dots\dots\dots(11)$$

From the experimental data on WPCs without clay, the measured value of E_c and E_m can be used and the calculated value of V_f used to compute $E_f \eta_L \eta_o$. This quantity should remain unchanged when clay is added to the matrix. Here, the densities of neat PP and WPCs containing 50wt% wood (but no layered silicate) were determined by a helium pycnometer and were found to be 920kg/m³ and 1120kg/cm³, respectively. Therefore, the volume fraction of fibers (V_f) can be calculated, and this gives a value of 38.39vol%. With modulus data available in both tension and flexure, values of $E_f \eta_L \eta_o$ can be calculated, and these are listed in Table 4-6; the coupling agent level here is 4wt% of wood. When the matrix becomes a PNC, appropriate V_f and E_m values can be introduced into equation (11) to predict the modulus of the WPC. These predictions are compared with experimental data, for both one-step and two-step compounding, in Figures 4-11 and 4-12. As can be seen from the figures, the values of the predicted modulus are close to the experimental values for two-step compounding. For one-step compounding, though, the measured matrix properties were inferior, and this is reflected in the smaller predicted WPC values; consequently, there is a slight mismatch with data. This says that the modified rule of mixtures can only be used as a rough guide for predicting the modulus values of WPCs.

Table 4-6 $E_f \eta_L \eta_o$ values for WPC samples containing 50wt% WF

	V_f %	E_m (GPa)	E_c (GPa)	$E_f \eta_L \eta_o$ (GPa)
Tension	38.39	1.26	4.26	9.074
Flexure	38.39	1.07	3.67	7.842

In closing this section, the results of TGA analysis showed that the thermal responses of the different WPCs depended only on the clay loading level and that the thermal stability of WPCs progressively increased in the presence of the layered silicate.

Figure 4-11 Measured and predicted tensile modulus of WPCs produced with different compounding procedures

Figure 4-12 Measured and predicted flexural modulus of WPCs produced with different compounding procedures

4.5 Conclusions

Based on the results of the experiments described here, the addition of 4wt% of PP-g-MA to WF in WPCs seems to be the optimum loading level of coupling agent necessary to provide good adhesion between PP and wood particulates. This amount of coupling agent not only increases the strength of the WPCs significantly (See Appendix I Table A1-3) but also increases the modulus of WPCs in the presence of increasing amounts of nanoclay (See Appendix I, Table A1-4). The addition of layered silicates to WPCs formulated with a 50wt% wood content progressively improves the modulus of WPCs. Thus, instead of increasing the wood content in the WPCs, one may add layered silicate to the polymer matrix. This has the added benefit of improved thermal stability of WPCs.

Since the final WPC is made up of a number of ingredients, different mixing protocols and extruder operating conditions can be employed, and these influence the final results; some of these results can be understood based on the concept of specific mechanical energy. Here, two different compounding processes were used, and it was found that introducing all the constituents into the extruder at the same time gave the best results. This result is, no doubt, related to the competition between wood and clay for the PP-g-MA that acts both as a coupling agent for the wood and as a dispersant for the clay. Producing WPCs by a one-step compounding process is also preferable from the viewpoint of minimizing processing costs.

The measured modulus data of WPCs can be understood based on a modified rule of mixtures. The measured modulus of WPC samples compounded with two steps was

found to be slightly lower than the modulus predicted by the rule of mixtures, while the measured modulus of WPC samples compounded with a one-step process was found to be slightly higher than the predicted modulus.

CHAPTER 5: PP-BASED WOOD-PLASTIC COMPOSITES REINFORCED WITH DIFFERENT AMOUNTS OF WOOD AND ORGANOCLAY

5.1 Objectives

To understand the effect of wood and nanoclay content on the mechanical properties of WPCs, composites were made by compounding 10, 20, 30 and 50wt% WF with a PP / clay nanocomposite matrix using a co-rotating twin-screw extruder.

5.2 Introduction

In this study, a PP/nanoclay master batch was diluted to give polymer nanocomposite pellets having varying percentages of clay, and these pellets were then compounded with WF and a fixed amount of PP-g-MA that acts as a coupling agent between wood and PP. The WPC pellets were finally injection molded into test specimens whose thermal and mechanical properties were measured and whose fracture surfaces were examined with the help of a scanning electron microscope (SEM). Results obtained were compared with results on WPCs containing additional WF but no clay. The goal was to determine the enhancement in the modulus of both the base polymer and the injection-molded WPCs. The modulus of WPCs can be predicted with a modified rule of mixtures while the maximum modulus of WPCs is predicted with the Halpin-Tsai Equation. Also, the peak mass release temperature (PMRT) in a TGA can be determined as a function of wood and organoclay content.

5.3 Experimental Details

WPCs were compounded with 10, 20, 30 and 50wt% of 80-mesh maple WF and PP-based PNCs using a Leistritz Mirco-27 co-rotating twin-screw extruder (operating at 85rpm)

with a K-Tron powder feeder and a pellet feeder. The detailed two step compounding procedure can be found in section 3.2.2.1. A master batch of PP and nanoclay (PolyOne Nanoblend™ 1001) was employed to first make PNC pellets having 0wt%, 2wt%, 4wt% and 10wt% of nanoclay, and the volume percentage of clay in the matrix for the clay was estimated to be 1.4vol%, 2.75vol%, and 7vol%, respectively. Then, these pellets were compounded with PP-g-MA and different amounts of WF using the same extruder to get WPCs containing 10, 20, 30 and 50wt% of WF in a matrix with 0, 2, 4 or 10wt% of organoclay. Also, fixed percentages of PP-g-MA pellets (Chemtura PolyBond® 3200) were mixed with the WF so that the amount of coupling agent was either 0% or 4% of the weight of WF compounded. In this manner, 20 different batches of WPCs containing 10, 20, 30 and 50wt% of WF and different amounts of clay and PP-g-MA were prepared. The compounded WPC pellets were dried and then injection molded using a Battenfeld injection molding machine to produce standard ASTM samples. In addition, the shear viscosity of WPCs was measured by a Rosand RH2000 capillary rheometer, and the temperature was controlled at 180°C.

The temperature / weight loss curves of WPCs samples were measured by TGA analysis (TA Instrument TGA Q500). Five milligrams of a WPC sample was cut from the WPC pellets. Samples were heated at a rate of 10°C/min and purged with air. Each TGA test was run at least twice.

5.4 Results and Discussion

It was found that, as expected, the shear viscosity of WPCs was a function of the wood content (see Figure 5-1) but was not affected by the clay in the matrix. The rapid increase

in viscosity with added WF, especially at low shear rates, is relevant to the phenomenon of melt fracture that is often observed during extrusion of WPCs, since this limits production rates.

A TEM picture of the nanocomposite containing 4wt% organoclay is shown in Figure 5-2. It is seen that the clay platelets are not exfoliated; rather, they are intercalated with PP. The mechanical properties of PNCs containing 0, 2, 4 and 10wt% of organoclay are listed in Table 4-2 in Chapter 4 which shows that the modulus of PNCs increases with the amount of organoclay in the matrix; the addition of 4wt% clay to PP gives a 51% increase of the flexural modulus.

Figure 5-1 Shear viscosity of WPCs containing different amounts of wood flour at different shear rates. (4wt% PP-g-MA to wood flour, no clay)

Figure 5-2 TEM Picture of a PNC Sample Containing 4wt% Clay (100000x)

The tensile strength of PNC-based-WPCs is shown in Figure 5-3. Since samples containing less than 30wt% WF did not break at 5% flexural strain, the flexural strength data are not reported here to avoid any misunderstanding. The effect of PP-g-MA and WF content on the strength of WPCs can be seen in the first and second data columns of Figure 5-3. It is evident that without the coupling agent the tensile strength decreases with WF content. In the presence of PP-g-MA, though, the tensile strength increases significantly with WF content (See Appendix I, Table A1-3); it almost doubles in the case of 50wt% WF as compared to sample without PP-g-MA. This is because PP-g-MA improves bonding between the WF and the PP. However, the relative increase in strength of WPCs depends on the amount of clay in the matrix. It is interesting to point out that without nanoclay, the

strength increases with the WF content. In the presence of nanoclay, the strength of WPCs first shows a trend of decreasing with WF content and then increases again at 50wt% of WF. This phenomenon has to be further investigated. The decrease in strength was unexpected since the loading level of PP-g-MA was kept proportional to the WF content. The explanation for this reduction in strength is provided by the SEM micrographs of the impact fracture surfaces of WPCs. As can be seen from Figure 5-4(a), for a WPC sample containing 4wt% of PP-g-MA, there are many broken wood fibers embedded in the fracture surface than there are fibers that have been pulled out. This means that the wood fiber bonds well to the neat PP. On the other hand, WPC samples of the same composition, but made with a PNC containing 4wt% of clay in the matrix, show significantly more fiber pull out as evidence by holes in the fracture surface, which can be seen in Figure 5-4(b). This may be because the affinity between silicate and maleic anhydride is stronger than the affinity between hydroxyl group on the wood surface and maleic anhydride.

Figure 5-3 Tensile strength of WPCs containing different amount of WF with and without PP-g-MA

(a)

(b)

Figure 5-4 WPCs contain 10wt% WF with 4wt%CA to WF, (a) no clay, 110x (b) 2wt% clay in matrix, 60x

Since the main application of WPCs is decking, flexural modulus of WPCs is the major concern. The flexural modulus of PNC-based WPCs is shown in Figure 5-5. The modulus of WPCs increases with WF content because the modulus of WF is much higher

than PP. The flexural modulus of WPCs shows a trend of increasing with the clay content in the matrix except for WPC containing 50wt% WF and 2wt% of clay in the matrix. This is because the amount of clay added in the matrix is only 2wt% of PP, which could be translated into only 1wt% of the total weight of WPCs. The effect of such a small amount of clay on modulus appears not to be very significant. The Fisher's least significance difference value is 0.15GPa at 50wt% of wood content (See Appendix II Table A1-4). Thus, the difference is significant only when 10wt% nanoclay present in the matrix. Also, it is suspected that there is some unknown low molecular weight compatibilizer in the master batch which decreases the modulus of the composites. This is because low molecular weight compatibilizers such as PP-g-MA are commonly used in PP-based PNCs to swell the gallery of nanoclay and thus improve the exfoliation of nano-particles. If organoclay powder and known compatibilizer are used instead of organoclay master batch, this phenomenon may not be observed.

Figure 5-5 Flexural modulus of WPCs containing different levels of WF, PP-g-MA and clay

On the other hand, when the loading level of organoclay increases to 10wt% of the matrix, the reinforcement effect from organoclay becomes more apparent. For example, When 5wt% of organoclay was added to the 50wt% WF-WPCs, (10wt% of the matrix), the flexural modulus of WPCs increased 18~20%. Adding nanoclay into WPCs could also reduce the loading level of WF in the WPCs. Generally, it is preferred to produce WPCs of high WF content because the price of WF is much lower than that of polymer. However, some process difficulties such as melt fracture and extrusion instability happen when the WF content exceeds 50wt%. Also, the rate of water absorption of WPCs may be increased significantly. This issue will be discussed in Chapter 6. By adding organoclay, these problems could be avoided and material performance increased, too.

Again, to determine if the improvement in WPC mechanical properties obtained as part of this research was what might reasonably be expected, the rule of mixture was used. According to this rule, the modulus of a continuous-fiber-reinforced composite is:

$$E_c = E_m V_m + E_f V_f \dots\dots\dots (2)$$

and equation (2) can be modified by including a length correction factor η_L and an orientation correction factor η_O as shown below:

$$E_c = E_f \eta_L \eta_o V_f + E_m (1 - V_f) \dots\dots\dots (11)$$

From the experimental data on WPCs without clay, the measured value of E_c and E_m could be used and the calculated value of V_f used to compute $E_f \eta_L \eta_o$. This quantity should remain unchanged when clay is added to the matrix. Here, the densities of neat PP and WPCs containing 10, 20, 30 and 50wt% wood (but no layered silicate) were determined by a helium pycnometer and were found to be 920, 950, 990, 1030 and 1120kg/m³,

respectively. Therefore, the volume fraction of fibers (V_f) can be calculated, and this gives a value of 5.8, 13.3, 21.3 and 38.39vol%, respectively at WF contents of 10, 20, 30 and 50wt%. With modulus data available in flexure, values of $E_f\eta_L\eta_o$ can be calculated, and these are listed in Table 5-1; the coupling agent level here is either 4wt% of wood or none. The theoretical moduli of WPCs with or without coupling agent were calculated-based on $E_f\eta_L\eta_o$ values with or without coupling agent, respectively. Also, two different theoretical moduli values were calculated based on $E_f\eta_L\eta_o$ of WPCs at 10 and 50wt% WF, respectively. When the matrix becomes a PNC, appropriate V_f and E_m values can be introduced into equation (11) to predict the modulus of the WPCs. Here, the E_m values are the moduli of PNCs containing different amounts of nanoclay. The results for the theoretical modulus and the experimental modulus are shown in Figure 5-6. The theoretical moduli shown in Figure 5-6(a) were calculated using $E_f\eta_L\eta_o$ of 10wt% of WF. This is because the theoretical modulus predicted by 10 wt% fiber modulus values fit the experimental values well when the WF content is less than 30wt%. The largest error is 16% and most of the errors are less than 10%. However, when the WF content increased to 50wt%, the theory did not fit the experimental data well, and the error increased to 30%. On the other hand, as it can be seen from Figure 5-6(b), the modulus predicted by $E_f\eta_L\eta_o$ of 50wt% WF fits the flexural modulus of WPCs containing 50wt% WF and different amount of clay well. Here, the flexural modulus predicted by this datum always overestimates the flexural modulus of WPCs with lower WF content by at least 15%. This error can be attributed to fiber alignment and fiber-fiber interaction effect in the composites. Since the shear viscosity of WPCs increases rapidly with WF content, the

flow pattern of WPCs containing different amounts of WF would be very different during injection molding. Therefore, the orientation of fibers can change with the WF content in the matrix. Also, in the modified rule of mixtures, the fiber-fiber interaction effect was not included in the equation. However, whenever the WF content increases, fiber-fiber interaction is likely to be more significant and therefore affect the flex modulus of WPCs. Thus, the modified rule of mixtures can only provide a rough estimate of the flexural modulus of WPCs. More realistic composites models need to be applied in the future.

Figure 5-6 (a)

Figure 5-6 (b)

Figure 5-6 A comparison between flexural modulus of WPCs calculated based on $E_f\eta_L\eta_o$ values of (a) 10wt% and (b) 50wt% WF

Table 5-1 $E_f\eta_L\eta_o$ values for WPC samples containing 10 and 50wt% WF with and without coupling agent (CA)

	CA	Wood Content (wt%)	V_f (%)	E_m (GPa)	E_c (GPa)	$E_f\eta_L\eta_o$ (GPa)
Flexure	N	10	6	1.07	1.31	5.049
Flexure	Y	10	5.8	1.07	1.33	5.549
Flexure	N	50	38.62	1.07	3.85	8.269
Flexure	Y	50	38.39	1.07	3.67	7.842

Besides the modified rule of mixtures, the tensile modulus of WPCs containing different amounts of clay and wood were predicted by the Halpin-Tsai Equation, too. In the Halpin-Tsai equation the moduli of matrix and wood fiber were considered to be 1.28 and 20GPa [81] respectively, while the modulus of the layered silicate was 178GPa [15]. According to the manufacturer's data, the aspect ratio of 80 mesh WF is three. The tensile modulus of polymer nanocomposites as predicted by the Halpin-Tsai equation is shown

in Figure 5-7. Since the layered silicates were not exfoliated and not aligned in the polymer matrix, the experimental value of PP-based nanocomposites was lower than the modulus predicted by the Halpin-Tsai equation, especially when the clay content is high. The moduli of WPCs were also predicted with the the Halpin-Tsai equation to see the difference between the theoretical prediction and experimental value. Here, two different values of the matrix E_m were applied. The modulus of WPCs are predicted by the Halpin-Tsai Equation either using the measured matrix modulus (Figure 5-8), or the theoretical maximum matrix modulus (Figure 5-9). It is worthwhile to note that in Figure 5-9, the Halpin-Tsai equation was applied twice. First, it was applied to calculate the theoretical maximum modulus of PP-based nanocomposites and the aspect ratio of layered silicate was assumed to be 100. Then, it was applied again to predict the modulus of WPCs containing different amount of wood and clay.

Figure 5-7 Modeling the modulus of PP-Clay nanocomposites by the Halpin-Tsai Equation

Figure 5-8 Tensile modulus predicted by the Halpin-Tsai equation using measured matrix modulus

Figure 5-9 Tensile modulus predicted by the Halpin-Tsai equation. The aspect ratio of clay is assumed to be 100.

It can be seen from Figures 5-8 and 5-9 that the Halpin Tsai equation fits the experimental values well when there is no clay added in the matrix. When nanoclay was added to the matrix, the modulus of WPCs increased with the clay content; however, it is much lower than that predicted by the Halpin-Tsai Equation. This is because clay was not exfoliated and aligned. In addition, wood fibers were not aligned either. The modulus reinforcement effect of clay decreases with clay content because layered silicate platelets are not easy to be exfoliated at high concentration. However, according to Figure 5-9, if nanoclay could be exfoliated and aligned well, the theoretical tensile modulus of WPCs containing 50wt% of wood and 10wt% of clay in the matrix could be as high as 8.23GPa which is close to the modulus of solid wood. The modulus of elasticity of solid wood is around 9~12GPa [142]. The modulus of elasticity predicted by the Halpin-Tsai equation clearly points out that by properly aligning clay and WF, the modulus of WPCs could be improved and made close to solid wood.

The results of TGA analysis are shown in Table 5-2. Since the results of WPCs with and without PP-g-MA but no clay did not show much difference, only data for samples containing PP-g-MA with / without 4wt% of clay in the matrix will be reported. It is seen that the peak mass release temperature (PMRT) (maximum temperature of dm/dT), increases with the wood content when there is no clay present. It is suspected that WF in the matrix forms a layer of char during the burning process and prevents mass release. On the other hand, when there is 4wt% of organoclay added to the matrix, the PMRT decreases with WF content. Although not shown in the table, the PMRT of WF is 325°C, and WF is completely burned out at 650°C. On the other hand, organoclay is much more stable than WF is; 70wt% of organoclay was not burned at the temperature of

800°C. Therefore, the PMRT of PP shifted from 306°C to 415°C in the presence of 4wt% of clay. Since the organoclay was intercalated in the PP matrix, it holds the polymer matrix better during the burning process. However, organoclay was not intercalated with WF and WF/PP microscopically, and it remained as two different phases. WF in the WPCs would therefore first be burned during the heating process. Therefore, the PMRT of PNC-based WPCs decreases with the WF content. Although PMRT decreases with WF content when organoclay is added, the PMRT of WPCs containing 50wt% of WF is still higher than the PMRT of WPCs without clay.

Table 5-2 Peak mass release rates of WPCs containing 0 and 4wt% of organoclay in the matrix

Clay to Matrix (wt%)	Wood (wt%)	Maximum of dm/dT (°C)	Clay to Matrix (wt%)	Wood (wt%)	Maximum of dm/dT (°C)
0	0	305.58	4	0	414.25
0	10	318.44	4	10	396.06
0	20	334.39	4	20	384.74
0	30	363.8	4	30	380.68
0	50	362.96	4	50	366.06

5.5 Conclusions

The following conclusions can be drawn from this chapter:

- The shear viscosity of WPCs doubles when WF content in the WPCs is increased from 0wt% to 50wt%.
- The strength of WPCs increases significantly with the aid of a coupling agent (PP-g-MA). The more WF present in the WPCs, the stronger the WPCs are.
- Nanoclay platelets are intercalated with the PP matrix. Microscopic pictures of impact fractured samples indicate that there are much more fibers pulled out when nanoclay is

added to the WPCs. This lowers the strength of WPCs.

- The flexural modulus of WPCs increases by at least 20% when 10wt% of organoclay is present in the matrix.
- When there is no nanoclay added to the matrix, the PMRT increases with WF content. PMRT decreases with the WF content when 4wt% of nanoclay is added to the matrix of WPCs.
- The modified rule of mixtures can be used as a guide to predict the modulus of WPCs.
- When the theoretical maximum modulus of nanoclay-reinforced PP as predicted by the Halpin-Tsai Equation is used to estimate the theoretical maximum modulus of WPCs made with 10wt% of nanoclay in the matrix, the WPCs modulus can be as high as 8GPa which is close to the modulus of solid wood.

CHAPTER 6 EFFECT OF THE COMPOUNDING PROCEDURE ON THE PROPERTIES OF PP-BASED WOOD -PLASTIC COMPOSITES CONTAINING NANOCLAY

6.1 Objectives

In Chapter 4, it was found that the addition of nanoclay would increase the stiffness of WPCs but the strength was decreased. Here, different compounding procedures are adopted to both maintain the strength and to decrease the rate of water absorption of WPCs. The strength reduction of WPCs is sought to be recovered by proper compounding and the stiffness of WPCs increased by adding nanoclay. A proper compounding procedure not only maintains the strength of WPCs, it also reduces the rate of water absorption of WPCs.

6.2 Sample Preparation

6.2.1 One Step Compounding

In these experiments, WF, nanoclay, PP and other additives were all fed into the hopper of the twin-screw extruder. The product was compounded WPCs containing 0, 2, 4, and 10wt% of layered silicate in the polymer matrix and, the amount of PP-g-MA in these experiments was a sum of two quantities: 4wt% of WF plus 3 times the weight of nanoclay [63, 68, and 70]. Additionally, three batches of WPCs are compounded with only 4wt% of PP-g-MA to wood to verify the effect of PP-g-MA to nanoclay. Each formulation of WPCs was compounded at 150rpm and 4.8kg/hr. To understand how screw geometry affects the properties of WPCs, these samples were compounded using both co-rotation and counter rotation screws. The screw design charts are shown in Figures 3-1 and 3-2 respectively. A detailed formulation of samples made with one step compounding is listed in Table 6-1.

6.2.2 Modified 2 Step Compounding

Instead of feeding all of the materials into the twin screw extruder at once, WF, PP, PP-g-MA and antioxidant are pre-compounded in the first step. It should be noted that the loading level of coupling agent is fixed at 4wt% of WF. Thus, three batches of WPCs were pre-compounded, which contain 52, 54 and 62.5wt% of WF. Nanoclay was introduced into the WPCs in the second step. Nanoclay and 3 times of PP-g-MA were compounded with pre-compounded WPC pellets using a twin screw extruder. The final product was compounded WPCs of 50wt% of wood, and it contained 2, 4, or 10wt% of layered silicate in the polymer matrix. In addition, another batch of WPCs contained 50wt% of wood and no clay and it was also passed through the extruder twice for comparison. In both steps, the total feeding rate was controlled at 4.8kg/hr while the screw speed was controlled at 150rpm. These samples were compounded using both co-rotation and counter rotation screws as well. A detailed formulation of samples made with the modified 2 step compounding procedure is listed in Table 6-2.

Table 6-1 Experimental matrix of WPCs with different amount nanoclay with and without excess amount of PP-g-MA. Samples are made with single step compounding.

Run #	Screw Rotation	Wood	Matrix (PP+ Clay + PP-g-MA)	PP-g-MA to Wood	PP-g-MA to clay ratio (Times)	Nanoclay to Matrix
1	Co	50%	50%	4%		0
2	Co	50%	50%	4%	3	2%
3	Co	50%	50%	4%	3	4%
4	Co	50%	50%	4%	3	10%
5	Co	50%	50%	4%	0	2%
6	Co	50%	50%	4%	0	4%
7	Co	50%	50%	4%	0	10%
8	Counter	50%	50%	4%		0
9	Counter	50%	50%	4%	3	2%
10	Counter	50%	50%	4%	3	4%
11	Counter	50%	50%	4%	3	10%

Table 6-2 Experimental matrix of WPCs with different amount nanoclay with and without excess amount of PP-g-MA. Samples are made with modified 2 step compounding.

Run #	Screw Rotation	Wood	Matrix (PP+ Clay + PP-g-MA)	PP-g-MA to Wood	PP-g-MA to clay ratio (times)	Nanoclay to Matrix	Pass
12	Co	52%	48%	4%		0	1
13	Co	54%	46%	4%		0	1
14	Co	62.5%	37.5%	4%		0	1
15	Counter	52%	48%	4%		0	1
16	Counter	54%	46%	4%		0	1
17	Counter	62.5%	37.5%	4%		0	1
18	Co	50%	50%	4%		0	2
19	Co	50%	50%	4%	3	2	2
20	Co	50%	50%	4%	3	4	2
21	Co	50%	50%	4%	3	10	2
22	Counter	50%	50%	4%		0	2
23	Counter	50%	50%	4%	3	2	2
24	Counter	50%	50%	4%	3	4	2
25	Counter	50%	50%	4%	3	10	2

6.3 Results and Discussion

The tensile modulus of WPCs made with one step compounding is shown in Figure 6-1. As can be seen from Figure 6-1, WPCs made without excess amount of PP-g-MA to nanoclay possess lower modulus than those made with excess amount of PP-g-MA. The enhancement of modulus is attributed to either the intercalation of clay or the excess amount of PP-g-MA and the differences in modulus values are statistically significant (See Appendix I, Table A1-5). From Chapter 4, it has been shown that the modulus and strength of the PP-g-MA used in this study are similar to those of PP. Thus, the modulus enhancement of WPCs can be an indication of the intercalation or exfoliation of nanoclay, and this enhancement is statistically significant in the presence of nanoclay (See Appendix I, Table 1-6). Similar studies have been done by Kim et al., for PP-nanoclay nanocomposites [143]. On the other hand, the modulus of WPCs made with counter rotation screw shows higher value than that made with co-rotation screw. This is probably due to the different geometry of the screws. The tensile strength of WPCs with and without excess amount of PP-g-MA to nanoclay is shown in Figure 6-2. The WPCs without excess amount of PP-g-MA show much lower tensile strength than those with excess PP-g-MA. Also, the tensile strength of WPCs decreases in the presence of nanoclay, and it appears that nanoclay attracts most of the PP-g-MA during compounding. This is consistent with results presented earlier in Chapter 4.

Figure 6-1 Tensile modulus of 50wt% wood WPCs reinforced with different amount of nanoclay. Samples are made with co-rotation or counter rotation screws.

Figure 6-2 Tensile strength of 50wt% wood WPCs reinforced with different amount of nanoclay. Samples are made with co-rotation or counter rotation screws.

Since nanoclay appears to attract most of the PP-g-MA during compounding, and since the strength of WPCs comes from the chemical reaction between WF and PP-g-MA, it is reasonable to compound PP, wood and PP-g-MA first in order to have PP-g-MA react with wood to see if the strength of WPCs can be better maintained. The tensile strength of WPCs made with different compounding procedures and different screw geometries is shown in Figures 6-3 and 6-4. It should be noted that at 50wt% PP-based WPCs pass

through the extruder twice for modified 2 step compounding in the absence of clay for comparison. Additionally, the first column in the figure represents strength of samples containing 52, 54 and 62.5wt% of WF, and the numbers above the column indicate the wood content as a weight percentage. As can be seen in Figures 6-3 and 6-4, the tensile strength of WPCs was maintained better by using a modified 2 step compounding scheme. For example, in the presence of 2wt% of clay, the strength of WPCs made with modified 2 step compounding is 20% higher than that made with single step compounding. In other words, the strength of WPCs does not decrease at low clay concentration when samples are compounding with a modified 2 step compounding process. The strength of WPCs containing 52, 54 and 62.5wt% WF is around 40 ~ 42MPa. The strength of WPCs does not change at similar PP-g-MA content. This is similar to the situation when WPCs contain no clay.

The moduli of WPCs made with single step compounding and modified 2 step compounding are shown in Figures 6-5 and 6-6, respectively. From Figure 6-5, it is found that different compounding procedures do not affect the modulus of WPCs which are compounded with co-rotation screws and the modulus of WPCs increases with clay content. The modulus of WPCs increases with wood content, too, but it is not easy to compound WPCs when the wood content is higher than 55% without using other additives. On the contrary, although WPCs processed with counter rotation screws show a higher modulus than when processed with co-rotation screws in single step compounding, the modulus of WPCs decreases when materials are passed through the extruder twice. This can be seen in Figure 6-6. This may be because passing WPCs through the extruder twice using counter rotation screws further destroys the micro-structure of WF. Therefore, in the current case, although modified 2 step compounding helps retain the tensile strength of WPCs, the

modulus of WPCs is decreased when WPCs are passed through the extruder twice using counter rotation screws which is undesirable. Because of this, the following discussion will be focused on the samples made with co-rotation screws.

Typical tensile fracture surfaces of WPCs made with single step compounding and modified 2 step compounding containing 2wt% of nanoclay in the matrix are shown in Figures 6-8 and 6-9 respectively. As can be seen from the figures, a sample processed with single step compounding shows a large area of fiber pullout while that processed with modified 2 step compounding shows less fiber pullout. Thus, these microscopic figures clearly explain why samples compounded with a modified 2 step compounding process possess higher strength.

Figure 6-3 Tensile strength of 50wt% wood WPCs reinforced with different amount of nanoclay and made with single step compounding or modified 2 step compounding. Samples are processed with co-rotation screws. The first data set is the strength of sample made in step one of modified 2 step compounding. The numbers above the columns are wood content.

Figure 6-4 Tensile strength of 50wt% wood WPCs reinforced with different amount of nanoclay and made with single step compounding or modified 2 step compounding. Samples are processed with counter rotation screws. The first data set is the strength of sample made in step one of modified 2 step compounding. The numbers above the columns are wood content.

Figure 6-5 Tensile modulus of 50wt% wood WPCs reinforced with different amount of nanoclay and made with single step compounding or modified 2 step compounding. Samples are processed with co-rotation screws. The first data set is the modulus of sample made in step one of modified 2 step compounding. The numbers above the columns are wood content.

Figure 6-6 Tensile modulus of 50wt% wood WPCs reinforced with different amount of nanoclay and made with single step compounding or modified 2 step compounding. Samples are processed with co-rotation screws. The first data set is the modulus of sample made in step one of modified 2 step compounding. The numbers above the columns are wood content.

The reversed notch Izod impact strength of WPCs made with one step compounding and modified 2 step compounding with co-rotation screws is shown in Figure 6-7. As can be seen from this figure, modified 2 step compounding helps retain the reversed notch Izod impact strength significantly as well. Again, the impact strength of WPCs does not decrease at low clay content. Thus, modified 2 step compounding not only helps retain tensile strength of WPCs but helps retain the impact strength of WPCs as well. Also, unlike tensile strength, the impact strength decreases with the loading level of WF. It can be seen in the figure that the impact strength of WPCs containing different loading levels of nanoclay and made with modified 2 step compounding is very similar to the impact strength of WPCs with different wood content.

Figure 6-7 Impact strength of 50wt% wood WPCs reinforced with different amount of nanoclay and made with single step compounding or modified 2 step compounding. Samples are processed with co-rotation screws. The first data set is the strength of sample made in step one of modified 2 step compounding. The numbers above the columns are wood content.

Figure 6-8 Tensile fracture surface of WPC sample containing 2wt% of clay in the matrix. Sample is made with single step compounding.

Figure 6-9 Tensile fracture surface of WPC sample containing 2wt% of clay in the matrix
Sample is made with modified 2 step compounding

The rate of water absorption of WPCs processed by single step compounding, modified 2 step compounding and different wood content is shown in Figure 6-10. Inevitably, due to the hydrophilic nature of clay, the rate of water absorption of WPCs increases with the loading level of clay. However, as can be seen in Figure 6-10, at similar clay loading levels, the modified 2 step compounding process not only helps maintain the strength of WPCs, it also decreases the rate of water absorption significantly, and these differences are statistically significant (See Appendix I, Table 1-5). These results are in line with previous assumptions. Nanoclay does not sequester the coupling agent which has already reacted with WF. As was mentioned previously, to simulate the process of modified 2 step compounding and no clay, a batch of WPCs containing 50wt% of wood was passed through the extruder twice. It can be found in Figure 6-10, even in the absence of clay, the rate of water absorption of WPCs is different. Passing WPCs through the extruder twice reduces the rate of water absorption of WPCs. This is because the particle

size of WF decreases with increasing processing time. This issue will be discussed in more detail in Chapter 7. Here, samples made with modified 2 step compounding and containing 2wt% clay in the matrix show even lower rate of water absorption than samples pass that through the extruder twice without nanoclay. This result is interesting and more work needs to be done to explain this issue.

Figure 6-10 Moisture absorption versus time for 50wt% wood WPCs reinforced with different amounts of nanoclay made with single step and modified 2 step compounding

The rate of water absorption of WPCs is listed in Table 6-3. Due to the differences in geometry of the samples, the moisture diffusion from the edge can not be neglected and thus the diffusion coefficient could not be determined. Therefore, the rate of water absorption was simply determined as the percentage weight gained per day from 5th day to 28th day of water immersion. Additionally, the rate of water absorption of WPCs containing different amounts of wood is listed in Figure 6-11. Moisture uptake of WPCs made with modified 2 step compounding and containing different amounts of clay is also shown in

this figure for comparison. When wood content increases in the composites, the rate of water absorption increases significantly. The statistical significance of these data sets is shown in Appendix I Table A1-7. In this study, wood content in the WPCs is the most important factor which affects the rate of water absorption. This is consistent with the study done by Steckel et al. [144]. When wood content of WPCs increased from 50wt% to 52wt%, the rate of water absorption of WPCs increased by a factor of 1.25. In addition, as can be seen in Figure 6-11, the rate of water absorption of WPCs containing 52wt% of wood is higher than that of WPCs containing 50wt% wood and 10wt% of nanoclay in the matrix. All of the issues above simply indicate that wood content is the major factor which affects the rate of water absorption of WPCs.

Table 6-3 Rate of water absorption exhibited by WPCs made with varying amounts of clay, wood and different procedures. The rate of water absorption is determined by the weight gain of samples from 5th day to 28th day.

	Single Step rate of water absorption (wt%/day)	STDEV (wt%)	Modified 2 Step rate of water absorption (wt%/day)	STDEV (wt%)
50wt% wood				
No Clay	0.062%	0.001%	0.056%	0.000%
2wt% Clay	0.068%	0.001%	0.053%	0.001%
4wt% Clay	0.093%	0.002%	0.056%	0.001%
10wt% Clay	0.200%	0.004%	0.071%	0.001%
52wt% wood	0.084%	0.002%		
54wt% wood	0.108%	0.001%		
62.5wt% wood	0.243%	0.001%

Figure 6-11 Moisture absorption versus time for WPCs made with modified 2 step compounding step 1 and step 2.

6.4 Exfoliation of Nanoclay

Previously, nanoclay was intercalated in the polymer matrix. If nanoclay palates are exfoliated in the polymer matrix, the mechanical properties, flame retardancy and foaming ability of WPCs may increase. However, it is not easy to exfoliate nanoclay in polypropylene or polyethylene. Since PP-g-MA was used as a compatibilizer to help the exfoliation of nanoclay in PP, it is possible to exfoliate nanoclay in PP-g-MA and make a master batch of polymer-clay nanocomposites. Similar approaches were adopted by Lee et al. [65] and Paul et al. [72] to make a polymer-clay nanocomposites master batch. Park et al. also successfully exfoliated nanoclay in polyethylene grafted maleic anhydride (PE-g-MA) and used it as a matrix material for WPCs. It has been found that if clay is exfoliated in the polymer well, the rate of burning is much lower than conventional composites or intercalated composites.

To confirm this result, nanoclay was compounded with PP-g-MA at different loading levels using the Leistritz Micro-27 twin screw extruder. The results are shown in Figures 6-12 to 6-15. As can be seen from these figures, nanoclay platelets were exfoliated uniformly in PP-g-MA matrix at 5wt% of nanoclay content. More nanoclay stacks are seen in the matrix when nanoclay content increases to 10wt% or 20wt%. Nevertheless, lots of nanoclay platelet stacks can still be seen in the PP-g-MA matrix. Based on these results, it is possible to compound PP-based WPCs with exfoliated nanoclay in the matrix with low clay concentration and follow up tests are need to be done to test the properties of WPCs reinforced with exfoliated nanoclay in the matrix.

Figure 6-12 PP-g-MA contains 5wt% of clay. The magnification is 30000x

Figure 6-13 PP-g-MA contains 5wt% of clay. The magnification is 108000x

Figure 6-14 PP-g-MA contains 10wt% of clay. The magnification is 30000x

Figure 6-15 PP-g-MA contains 20wt% of clay. The magnification is 30000x

6.5 Summary

In summary, there are two ways to increase the modulus of WPCs. One is to increase WF content in WPCs, and the other one is to add a high stiffness filler such as nanoclay. Increasing the loading level of WF increases the modulus of WPCs, but high wood content results in much higher rate of water absorption and process difficulties. Both issues are undesirable, especially the high rate of water absorption which results in dimensional changes. Also, though the tensile strength does not change with increasing wood content, the Izod impact strength decreases slightly. On the other hand, the modulus of 50wt% wood WPCs increases by adding even a small amount of nanoclay and excess amount of PP-g-MA in the matrix. It is necessary to add excess amount of PP-g-MA during compounding to help the exfoliation of nanoclay and thus improve to modulus of WPCs. By doing this, the modulus of WPCs increases, and process difficulties can be avoided.

However, due to the hydrophilic nature of nanoclay the rate of water absorption also increases with the loading level of nanoclay. Additionally, nanoclay will attract PP-g-MA during compounding. If all of the components are fed into the extruder at once and single

step compounding is done, the tensile and impact strengths of WPCs decrease dramatically with the loading level of nanoclay. This is because most of the PP-g-MA is taken up by nanoclay during compounding. If proper compounding procedures are adopted, the tensile and impact strengths of WPCs can be much better maintained. In this study, WPCs were compounded with either co-rotation screws or counter rotation screws. In both cases, modified 2 step compounding maintained the strength of WPCs significantly better than with single step compounding. Nevertheless, passing WPCs through the extruder twice with counter rotation screws led to a decrease of modulus. The reason for this issue has to be further investigated.

If WF is compounded with PP-g-MA in the first step and then compounded with nanoclay plus excess amount of PP-g-MA next using co-rotation screws, the tensile and impact strength reduction can be decreased without affecting the modulus of WPCs. In the present case, the strength reduction of WPCs went from 18% to almost none at 2wt% of clay loading level. At 10wt% of clay loading, the tensile strength reduction of WPCs decreases from 28% to 13%. Additionally, samples made with modified 2 step compounding show much lower rate of water absorption than with the use of single step compounding. As mentioned previously, although increasing WF content could increase the modulus of WPCs, the rate of water absorption increases dramatically with increase wood content. When WF content increases from 50wt% to 52wt%, the rate of water absorption of WPCs containing 52wt% of WF is higher than that of 50wt% wood WPCs containing 10wt% nanoclay in the matrix and made with single step compounding.

Adding nanoclay into WPCs by modified 2 step compounding is a better choice than increasing the wood content in the WPCs to improve the modulus of WPCs because increasing wood content is the major factor which leads to high rate of water absorption.

High wood content also results in process difficulties such as melt fracture. These issues can be avoided by adding nanoclay into the polymer matrix of WPCs. In this way, WPCs of higher modulus and relatively lower rate of water absorption can be produced.

Currently, the prices of nanoclay and coupling agent are around 2.50 USD/lb and 2 USD/lb, respectively. This is much higher than that of WF (9 cents/lb) and PP (85cents/lb). Therefore, the price of nanoclay reinforced WPCs will be higher than that without nanoclay. But the improvement in the properties of WPCs may allow these WPCs to be used in applications other than decking.

CHAPTER 7 EFFECT OF PROCESSING VARIABLES ON WATER ABSORPTION BY PP-BASED WOOD-PLASTIC COMPOSITES

7.1 Objectives

In Chapter 6, it was found that the rate of water absorption of WPCs decreases when WPCs are passed through the extruder twice. Thus, the rate of water absorption appears to be a function of processing variables. To investigate this further, a series of experiments was done to relate the rate of water absorption of WPCs to process variables of a twin screw extruder. This chapter was also published as a conference proceeding paper in the 9th International Conference on Wood and other Natural Fiber Plastic Composites held in Madison, WI.

7.2 Introduction

Although WPCs are widely used as decking materials today, they are susceptible to dimensional changes due to water absorption, and repeated cycles of moisture absorption and desorption can result in the loss of mechanical integrity. A partial solution to the problem is the addition of a coupling agent that not only increases WPC strength but also decreases the rate of water absorption. In this chapter, it will be shown that the effectiveness of the coupling agent can be increased by varying extrusion process conditions. PP-based WPCs were compounded using a twin screw extruder and injection molded into test specimens. The variables that were changed included extruder screw speed, screw geometry and feed rate, all of which influenced the residence time in the extruder.

Again, since wood particulates are polar (hydrophilic), water is absorbed from the atmosphere, and this results in dimensional changes and fungus growth [18]. As a consequence, the durability of WPCs can be reduced. A possible solution to this problem is the introduction of additives like PP-g-MA that have anhydride groups which can react

with the hydroxyl groups on the surface of WF and occupy sites where moisture might ordinarily have resided. Note that PP-g-MA is already added to PP-based WPCs to act as a coupling agent since it improves composite strength by promoting adhesion between wood and the non-polar (hydrophobic) PP. Thus, the incorporation of an optimum amount of PP-g-MA can serve both purposes.

The extent and manner of water absorption by WPCs can be determined in a variety of ways. A sample may either be exposed to air of specified relative humidity or be immersed in water to determine both the rate of moisture absorption and the equilibrium moisture content and, thus, the diffusion coefficient [144-148]. Some researchers also test WPCs in weather chambers that simulate real weathering conditions [149-155].

Although different pieces of compounding equipment can be employed to make WPCs [148, 156], the use of a twin screw extruder is standard in the industry, and its use gives composites having a high modulus and a low rate of water absorption. Surprisingly, though, not much research has been done to understand the effect of process variables of a twin screw extruder on the moisture absorption properties of WPCs [157, 158]. These variables include feed rate, screw speed, barrel temperature and screw geometry. This apparent neglect of process variables may be because the mechanical properties of WPCs are not sensitive to these variables [157, 158]. In this chapter, the influence of extruder process variables was examined by compounding eighteen batches of WPCs by changing the process variables. The rate of water absorption was determined with the help of a “blot and weigh” method to see if the rate of water absorption of WPCs was affected by the process variables.

7.3 Experimental Details

WPC samples were compounded using a Leistritz Micro-27 twin-screw extruder; half the samples were processed with co-rotation screws, and the other half were processed with counter-rotation screws. The experimental matrix is listed in Table 7-1, while the designs of the co-rotation and counter-rotation screws are shown in Figures 3-1 and 3-2, respectively. The total feeding rate was controlled at 2.4kg/hr, and all the samples contained 50wt% WF and the screw rotation speed was fixed at either 85rpm or 150rpm. As mentioned in Table 7-1, some of the WPC samples that were compounded at 85rpm were passed through the extruder twice to investigate the effect of doubling the residence time on the properties of WPCs. WPC strands emerging from the die were cooled in a water bath and then pelletized for further processing.

To determine if processing conditions altered the size distribution of the wood particulates in the WPCs, the impact samples from each batch of WPCs were treated with hot xylene to remove the PP matrix. After the matrix was dissolved, the magnetic stirrer was stopped while the hot plate was kept on for a further 40 minutes. During this time, the WF settled to the bottom of flask, and the supernatant was drained. The precipitate was then diluted with fresh xylene to prevent any remaining PP from coming out of solution during filtration. The mixture was boiled again and hot filtered to separate WF from the solution. The extracted WF was finally oven dried at 70°C for 48 hours. The extracted WF from each batch was dusted on carbon tapes and then observed using a Hitachi S-4700 FESEM to obtain the morphology of WF. In addition, the particle size distribution of WF was analyzed with a Shimadzu SALD-3101 particle analyzer. For this instrument, the refractive index was set at 1.7 and isobutyl alcohol was used as a dispersing agent to prevent particle aggregation. Before making measurements, the solution was mixed with a

circulation pump and sonicated with an ultrasonicator for one minute. The tests were repeated three times to ensure that ultrasonication did not affect the particle size distribution.

The optical properties of the WPCs were measured using a Macbeth Color-eye 7000 color meter. These tests were conducted courtesy of GE Plastics in Washington, WV. The results are presented in CIELab color space (L^* , a^* , b^*). Here, L^* means lightness and L^* ranges from 0 (black) to 100 (white). An impact sample was chosen from each batch of samples, and the color was measured at three different locations. The average value of lightness is reported here.

Finally, the IR spectrum of WF was obtained using a Perkin Elmer Spectrum One FTIR and employing oven-dried IR-grade potassium bromide as diluent. Around 1mg of WF was mixed with KBr powder using a mortar and pestle and then compressed into a disk. Typically, the samples were scanned about 100 times with a resolution of 4 cm^{-1} .

Table 7-1 Composition of various PP/WF composites. Samples were made with both co rotation and counter rotation screws. 18 batches of samples were compounded

Run	Screw RPM	Pass	Wood (wt%)	AO (wt%)	PP-g-MA (wt%) in Wood
1	85	1	50%	0.10%	0%
2	85	1	50%	0.10%	2%
3	85	1	50%	0.10%	4%
4	85	2	50%	0.10%	0%
5	85	2	50%	0.10%	2%
6	85	2	50%	0.10%	4%
7	150	1	50%	0.10%	0%
8	150	1	50%	0.10%	2%
9	150	1	50%	0.10%	4%

7.4 Results and Discussion

The tensile modulus values of the 50wt% wood WPCs but containing different amounts of PP-g-MA are shown in Figure 7-1; corresponding results for tensile strength

and impact strength are presented in Figures 7-2 and 7-3 respectively. It can be seen that the tensile modulus lies between 4GPa and 5GPa, with the counter rotating screws giving a slightly higher modulus under the same processing conditions and coupling agent content. On the other hand, the tensile strength appears not to depend on the processing conditions employed. Though, as expected, tensile strength values do increase as the coupling agent content is increased. The reversed notch Izod impact strength of WPCs also increases with the loading level of PP-g-MA, but counter rotating screws give lower values, and this is expected since stiffer materials usually possess lower impact strength.

Figure 7-1 Tensile modulus of WPCs made by different processes. E2 means 2 pass.

Figure 7-2 Tensile strength of WPCs made by different processes. E2 means 2 pass.

Figure 7-3 Reversed notch Izod impact strength of WPCs made with different processes.

The increase in moisture content as a function of time is shown in Figure 7-4 for WPC samples made with co-rotating screws; results for samples made with counter-rotating screws are presented in Figure 7-5. The rate of water absorption between the 3rd and the 36th day of water immersion and the equilibrium moisture content obtained from these figures are listed in Table 7-2. It should be noted that data are not presented for the case of 4wt% coupling agent and 150rpm screw speed for co-rotating screws because of experimental difficulties resulting from the high melt flow index of PP-g-MA. As can be seen from Figures 7-4 and 7-5, the rate of water absorption depends on the coupling agent, screw speed and material residence time in the extruder. As expected, the rate of water absorption decreased with an increase in PP-g-MA loading level due to reaction between hydroxyl groups on the WF surface and the maleic anhydride. Also, the chemical bonds formed between PP-g-MA and the wood fiber form a mass transfer barrier that retards diffusion of water molecules to the interior of the WF. However, as can be seen from Table 7-2, the presence of the coupling agent does not significantly alter the equilibrium moisture content for samples processed with either screw type. The likely reason for this is that wood is a porous medium, and as many as 99% of the hydroxyl groups lie on the inside

pores [23, 24]. The size of these pores ranges from 40 Å to 40 µm [25], and there is not enough time for PP-g-MA to react with hydroxyl groups inside these pores during compounding. However, water molecules can access these hydroxyl groups during the long term exposure in the absorption test.

Table 7-2 Rate of water absorption and equilibrium moisture of WPCs. The numbers in parenthesis are standard deviation.

PP-g-MA to wood (wt%)	Co Rotation	pass	Rate of Water Absorption (wt%/day)	Equilibrium moisture content (wt%)	Counter Rotation	Pass	Rate of Water Absorption (wt%/day)	Equilibrium moisture content (wt%)
0	85rpm	1	0.234 (0.001)	12.81 (0.01)	85rpm	1	0.249 (0.003)	12.36 (0.02)
0	85rpm	2	0.203 (0.002)	12.68 (0.06)	85rpm	2	0.199 (0.001)	12.06 (0.02)
0	150rpm	1	0.141 (0.0005)	11.25 (0.03)	150rpm	1	0.22 (0.001)	11.65 (0.02)
2	85rpm	1	0.099 (0.001)	12.02 (0.03)	85rpm	1	0.113 (0.002)	11.74 (0.02)
2	85rpm	2	0.090 (0.001)	11.87 (0.02)	85rpm	2	0.085 (0.0004)	11.11 (0.03)
2	150rpm	1	0.068 (0.001)	10.76 (0.01)	150rpm	1	0.091 (0.001)	10.76 (0.02)
4	85rpm	1	0.081 (0.001)	12.06 (0.03)	85rpm	1	0.078 (0.001)	11.59 (0.02)
4	85rpm	2	0.068 (0.0003)	11.84 (0.0002)	85rpm	2	0.068 (0.0004)	11.03 (0.03)
4	150rpm	1	N/A	N/A	150rpm	1	0.072 (0.001)	11.01 (0.06)

Figure 7-4 Moisture content as a function of time for WPCs made with co-rotation screws

Figure 7-5 Moisture content as a function of time for WPCs made with counter-rotation screws

Concerning the influence of screw rpm or residence time, Figures 7-4 and 7-5 say that increasing either quantity decreases the rate of water absorption by 10% ~ 40% at a fixed PP-g-MA level. For co-rotation screws, in particular, WPCs processed with the higher screw speed show a much lower rate of water absorption than other samples with the same coupling agent content, and this is true even in the absence of PP-g-MA. Indeed, WPCs compounded at 150rpm using co-rotating screws and without a coupling agent possess a lower rate of water absorption than similar samples processed at 85rpm and containing 2wt% PP-g-MA. Possible reasons for this behavior are discussed later. Note that in the case of counter-rotating screws, increasing residence time seems to be more important than increasing screw speed.

To understand if changing processing conditions lead to changes in the structure of WPCs, the results of measuring the average particle size are shown in Figures 7-6(a) and 7-6(b). A clear trend can be seen from Figure 7-6(a) which displays data for co-rotating

screws: a high screw speed (150rpm) and a long residence time (85rpm, 2 pass) reduce the size of WF, with the particle size of WF processed with the longer residence time being finer than for the one processed with the higher screw speed. This finding is not unreasonable, and says that some of the energy added to the composite during processing results in particulate fracture. Separately, other researchers have reported that finer WF particulates tend to reduce the water absorption rate of WPCs [144]. Thus, while the results in this study are consistent with those available in the literature, they do not explain why finer particulates result in a reduction in the rate of moisture absorption.

Figure 7-6 (a) Particle size of WF extracted from WPCs processed with co-rotation screws

Figure 7-6 (b) Particle size of WF extracted from WPCs processed with counter-rotation screws

Everything else being equal, the average size of WF is smaller when the WPCs are processed with co-rotation screws, and this means that the co-rotation screws provide more severe agitation as compared to the counter- rotating screws. This is not intended to be a general statement, and is true only for the screw designs shown in Figures 3-1 and 3-2.

The results of color measurement shown in Figures 7-7(a) and 7-7(b) indicate that samples processed with co-rotating screws are darker than those processed with counter-rotating screws under the same process conditions. This is because higher L^* values mean greater lightness. This again indicates that the co-rotation screws used in this work are more severe than the counter-rotating screws. Also, passing WPCs through the extruder twice made WPCs darker than when processed with a higher screw speed. Overall, though, the differences in lightness are small, and the appearance of all the sample batches was acceptable.

Figure 7-7 (a) Lightness of WPCs processed with co-rotation screws

Figure 7-7 (b) Lightness of WPCs processed with counter rotation screws

Since the laser particle analyzer assumes that each particle is a sphere, and since wood particulates are actually cylindrical, an optical microscope was used to confirm the results from the laser particle analyzer. A square sample of 12.7 mm x 12.7 mm was taken from an impact specimen. Samples were cut 25.4 mm away from the injection point and fine polished using sand paper and an aluminum oxide suspension. A schematic diagram illustrating the location from where the sample is collected is shown in Figure 7-8. Typical optical micrographs of WPCs processed under different conditions are shown in Figures 7-9(a) to 7-9(c). As can be seen from these figures, the particulate sizes in WPCs processed at 85rpm and 1 pass are coarser than those processed at high screw speed or with a longer residence time. Also, WPCs processed with a long residence time result in the finest particle size among the three different conditions. This is consistent with the results provided by laser particle analyzer.

Figure 7-8 Schematic diagram of sample collection for optical microscopy

Figure 7-9(a) 85rpm, and 1pass

Figure 7-9 (b) 150rpm and 1 pass

Figure 7-9 (c) 85rpm and 2 pass

Figure 7-9 Optical microscope pictures of WPCs processed with co-rotation screws and no coupling agent. Magnification is 20X

The density of WPCs was measured to see if the WF has been changed in any way during compounding. The density was determined simply by dividing the weight of a WPC sample by its volume. Results are shown in Table 7-3. It is found that the density of most WPCs is around $1080 \sim 1090 \text{ kg/m}^3$ except in the case of samples made with the co-rotating screws at the higher screw speed of 150rpm. Recall that these samples are the ones which exhibit much lower rate of water absorption and equilibrium moisture. It is speculated that the co-rotating screws, being the more severe ones, caused a larger increase in temperature inside the extruder during compounding, and this resulted in a loss of some hydrophilic volatile organic compounds from the WF [20]. The density of the sample processed with co-rotation screws at 150rpm and with 4wt% PP-g-MA loading level is also provided in Table 7-3, and it is around 1080 kg/m^3 . The reason is that the viscosity of WPCs decreases with the loading level of PP-g-MA and the WPCs melt leaked from the vent port and eventually plugged it. Thus the density of this sample is higher than that of samples processed under similar processing conditions. This data might explain the lowered density

and also the decreased rate of water absorption of WPCs processed with co-rotating screws.

Obviously, additional studies need to be done to determine the truth of this explanation.

Table 7-3 Density of WPCs made with different compounding processes. The numbers in parenthesis are standard deviation.

PP-g-MA to wood (wt%)	Co Rotation	pass	Density (kg/m ³)	Counter Rotation	pass	Density (kg/m ³)
0	85rpm	1	1089 (2)	85rpm	1	1083 (1)
0	85rpm	2	1084 (2)	85rpm	2	1086 (1)
0	150rpm	1	1064 (2)	150rpm	1	1082 (1)
2	85 rpm	1	1090 (1)	85rpm	1	1086 (1)
2	85rpm	2	1090 (2)	85rpm	2	1088 (1)
2	150rpm	1	1065 (1)	150rpm	1	1080 (1)
4	85rpm	1	1088 (3)	85rpm	1	1086 (2)
4	85rpm	2	1089 (2)	85rpm	2	1088 (1)
4	150rpm	1	1081 (2)	150rpm	1	1086 (2)

7.4.1 Statistical Analysis

Since the experiments are planned as a three factor factorial design with fixed effect, the data could be analyzed by statistics to ensure the results are statistically significant. In this analysis, only the samples containing 0wt% and 2wt% of PP-g-MA are included in the analysis to avoid interference from samples processed with co-rotation screws, 150rpm and 4wt% PP-g-MA. The analysis of variance (ANOVA) is listed in Table 7-4. All of the *F* values listed in Table 7-4 are much larger than the critical *F* value. Thus, every variable including screw geometry, processing methods, and PP-g-MA content is statistically significant. It also can be found from the *F* value that coupling agent is the most important of the three variables.

Table 7-4 ANOVA Table of WPCs processed with different processing methods and different PP-g-MA loading level

	df	SS	MS		<i>F</i>	Critical <i>F</i>
A: Screw geometry	1	3.715E-07	3.715E-07	MS _a /MS _e	1948.092	4.2597
B: Processing methods	2	1.179E-06	5.893E-07	MS _b /MS _e	3090.053	3.4029
C: PP-g-MA content	1	1.224E-05	1.224E-05	MS _c /MS _e	64171.613	4.2597
AxB	2	4.676E-07	2.338E-07	MS _{ab} /MS _e	1225.963	3.4028
AxC	1	8.614E-08	8.614E-08	MS _{ac} /MS _e	451.729	4.2597
BxC	2	1.862E-07	9.309E-08	MS _{bc} /MS _e	488.137	3.4028
AxBxC	2	1.502E-07	7.511E-08	MS _{abc} /MS _e	393.856	3.4028
Error	24	4.577E-09	1.907E-10			

7.5 FTIR Analysis

Since the addition of PP-g-MA decreases the rate of water absorption dramatically, it is of interest to examine the infra red spectrum of WF with and without PP-g-MA after compounding. Before carrying out the measurements, WF extracted from WPCs was pre-dried in an oven at 80°C to ensure that the moisture content was less than 1wt%. Typical spectra are shown in Figure 7-10. Unfortunately, no difference can be seen between the two IR spectra because WF itself contains ester groups. Thus, the esterification reaction between hydroxyl groups and maleic anhydride cannot be seen by FTIR [159]. The morphologies of WF are also observed by a scanning electron microscope. WF extracted from WPCs was lightly dusted on a carbon tape using a needle. Typical SEM pictures of WF taken from WPCs made with / without PP-g-MA are shown in Figures 7-11 (a) and 7-11 (b), respectively. As can be seen from Figure 7-11 (a), there are only a few aggregates in the WF treated with PP-g-MA. On the other hand, WF tends to form aggregates in the absence of PP-g-MA which can be seen clearly in Figure 7-11 (b); this is possibly because

the hydroxyl groups on the surface of WF form hydrogen bonds and attract each other [18].

Therefore, adding PP-g-MA definitely changes the chemical nature of the surface of WF.

Figure 7-10 IR spectra of WF extracted from WPCs

Figure 7-11 (a)

Figure 7-11 (b)

Figure 7-11 WF extracted from samples (a) with PP-g-MA, and (b) without PP-g-MA. Samples are processed with counter rotation screws at 150rpm

7.6 Conclusions

In summary, while a change of extrusion processing variables does not significantly affect the tensile strength and modulus of WPCs, it does affect the moisture absorption behavior. A long residence time and higher screw speeds not only result in smaller particulate sizes in the compounded WPCs, but also in a lower rate of water absorption. The reduction in moisture absorption rate ranges from 10% to 40%, and this happens without a change in the mechanical properties of the WPCs. It is found that the density of the WPCs is decreased under severe compounding conditions, and this offers a clue to the reason for the observed reduction in the rate of water absorption. It is speculated that moisture absorption rate decreases when severe compounding conditions are employed because these cause the loss of hydrophilic volatile organic compounds contained in the WPCs. The data were analyzed with analysis of variance (ANOVA) table and all of the experiments are statistically significant.

CHAPTER 8 CONCLUSIONS

In summary, several accomplishments have been achieved:

1. The tensile and flexural moduli of WPCs were improved by adding nanoclay, a high stiffness filler. However, the strength of WPC decreased and the rate of water absorption increased in the presence of nanoclay. This happens even though the nanoclay platelets were intercalated in the polymer matrix rather than exfoliated.
2. When different wood contents and amount of nanoclay were used to formulate the composites, the enhancement in modulus of WPCs could be predicted by the rule of mixtures. The maximum enhancement in modulus of WPCs is determined by applying the Halpin-Tsai Equation. If WF and nanoclay platelets are aligned, the modulus of WPCs can potentially be as high as 9GPa. This is similar to solid wood.
3. The reduction of tensile strength of WPCs reinforced with nanoclay can be partially recovered by changing the compounding procedure. Additionally, the rate of water absorption is reduced as well. WPCs with higher modulus than WPCs without nanoclay and similar strength to WPCs without nanoclay can be produced in this way.
4. By changing the processing variables such as screw speed and residence time, the rate of water absorption of WPCs can be reduced. A long residence time or a high screw speed help to reduce the rate of water absorption of WPCs. The moisture absorption rate decreases by as much as 10% to 40%.

5. By proper compounding, it is possible to prepare WPCs containing nanoclay that have improved modulus while containing strength and without increasing moisture absorption.

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Appendix I Statistical Analysis

The statistical significance of WPCs reinforced with nanoclay was analyzed by the analysis of variance (ANOVA) technique. The ANOVA tables of each section are listed for the following sections.

Table 4-2 Mechanical properties of PNCs prepared by diluting the Nanoblend™ 1001 master batch

Clay Content (wt%)	Organoclay Content, vol% (Estimated)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Density (kg/m ³)
0	0	1.26 ± 0.02	29.59 ± 0.09	1.07 ± 0.02	35.11 ± 0.11	911.8
2	1.43	1.41 ± 0.13	28.02 ± 0.12	1.36 ± 0.03	39.89 ± 0.46	917.9
4	2.75	1.53 ± 0.06	30.04 ± 0.35	1.62 ± 0.01	43.51 ± 0.09	930.8
10	7.00	1.96 ± 0.07	31.47 ± 0.36	2.06 ± 0.01	47.42 ± 0.1	947.1
20	14.57	2.65 ± 0.18	30.70 ± 0.55	2.72 ± 0.06	50.26 ± 0.19	982.6

Table A1-1(a) ANOVA table of PP reinforced with nanoclay, tensile modulus

Source	df	SS	MS	F	
Total	24	6.163025			$F_{0.05,4,20}=2.866$
Among	4	5.912144	1.478036	117.8275	
Within	20	0.250881	0.012544		

Ans: $F = 117.8275 > F_{0.05, 4, 20} = 2.866$, Significant

Table A1-1(b) ANOVA table of PP reinforced with nanoclay, flexural modulus

Source	df	SS	MS	F	
Total	24	8.393817			$F_{0.05,4,20}=2.866$
Among	4	8.384687	2.096172	4591.835	
Within	20	0.00913	0.000456		

Ans: $F = 4591.84 > F_{0.05, 4, 20} = 2.866$, Significant

Table 4-4. Mechanical properties of mixtures of PP and PP-g-MA

PP-g-MA Content (wt%)	Tensile Strength (MPa)	Tensile modulus (GPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)
2.4kg/hr 85rpm				
0%	29.59 ± 0.09	1.26 ± 0.02	35.11 ± 0.11	1.07 ± 0.02
10%	26.31 ± 0.16	1.34 ± 0.04	34.05 ± 0.89	1.08 ± 0.03
17%	25.96 ± 0.13	1.34 ± 0.07	33.64 ± 0.09	1.06 ± 0.02
38%	26.02 ± 0.05	1.40 ± 0.07	33.91 ± 1.56	1.07 ± 0.06
100%	24.93 ± 0.17	1.37 ± 0.02	35.16 ± 0.59	1.04 ± 0.03
4.8kg/hr 150rpm				
0%	29.59 ± 0.09	1.26 ± 0.02	35.11 ± 0.11	1.07 ± 0.02
10%	25.98 ± 0.31	1.33 ± 0.03	33.46 ± 0.12	1.04 ± 0.01
17%	25.80 ± 0.07	1.32 ± 0.03	33.34 ± 0.10	1.05 ± 0.01
38%	26.10 ± 0.09	1.37 ± 0.06	35.01 ± 0.41	1.08 ± 0.02
100%	24.93 ± 0.17	1.37 ± 0.02	35.16 ± 0.59	1.04 ± 0.03

Table A1-2(a) ANOVA table of PP/PP-g-MA blends, tensile modulus at 2.4kg/hr, 85rpm

Source	df	SS	MS	F	
Total	24	0.114056			$F_{0.05, 4, 20}=2.866$
Among	4	0.051135	0.012784	4.06337	
Within	20	0.062921	0.003146		

Ans: $F = 4.063 > F_{0.05, 4, 20}=2.866$, significant

Table A1-2(b) ANOVA table of PP/PP-g-MA blends, flexural modulus at 2.4kg/hr, 85rpm

Source	df	SS	MS	F	
Total	24	0.031785			$F_{0.05, 4, 20}=2.866$
Among	4	0.005105	0.001276	0.95677	
Within	20	0.02668	0.001334		

Ans: $F = 0.95677 < F_{0.05, 4, 20}=2.866$, insignificant

Table A1-2(c) ANOVA table of PP/PP-g-MA blends, tensile modulus at 4.8kg/hr, 150rpm

Source	df	SS	MS	F	
Total	24	0.077827			$F_{0.05, 4, 20}=2.866$
Among	4	0.038974	0.009744	5.015581	
Within	20	0.038853	0.001943		

Ans: $F = 5.015581 > F_{0.05, 4, 20}=2.866$, significant

Table A1-2(d) ANOVA table of PP/PP-g-MA blends, flex modulus at 4.8kg/hr, 150rpm

Source	df	SS	MS	F	
Total	24	0.013365			$F_{0.05, 4, 20}=2.866$
Among	4	0.004806	0.001201	2.807013	
Within	20	0.00856	0.000428		

Ans: $F = 2.807 < F_{0.05, 4, 20} = 2.866$, insignificant.

Table A1-3 ANOVA table of tensile strength of WPCs with different amounts of PP-g-MA

Source	df	SS	MS	F	
Total	19	1305.126			$F_{0.05, 3, 16}=3.239$
Among	3	1304.05	434.6833	6463.932	
Within	16	1.07596	0.067248		

Ans: $F = 6463.932 > F_{0.05, 3, 16} = 3.239$, significant

Table A1-4 ANOVA table of tensile modulus of WPCs reinforced with different amounts of nanoclay. PP-g-MA is fixed at 4wt% to wood

Source	df	SS	MS	F	
Total	19	1.440179			$F_{0.05, 3, 16}=3.239$
Among	3	1.258643	0.419548	36.97771	
Within	16	0.181535	0.011346		

Ans: $F = 36.978 > F_{0.05, 3, 16} = 3.239$, significant

Fisher's least significance difference (LSD) = $t_{0.025, 16} * \sqrt{2MSe/n} = 0.148219$

Table A1-5 ANOVA table of tensile modulus of WPCs reinforced with different amounts of nanoclay with and without excess amount of PP-g-MA in the matrix

Source	df	SS	MS	F	
Total	44	16.50118			$F_{0.05, 2, 42}=3.2199$
Among	2	6.514018	3.257009	13.69702	
Within	42	9.987161	0.23779		

Ans: $F = 13.697 > F_{0.05, 2, 42} = 3.2199$, significant

Table A1-6 ANOVA table of rate of water absorption of WPCs processed with single step and modified 2 step compounding

Source	df	SS	MS	<i>F</i>	$F_{0.05, 1, 22}=4.301$
Total	7	5.06E-06			
Among	1	1.3E-06	1.3E-06	7.61630331	
Within	22	3.76E-06	1.71E-07		

Ans: $F = 7.616 > F_{0.05, 1, 22} = 4.301$, significant

Table A1-7 ANOVA table of rate of water absorption of WPCs processed with modified 2 step compounding and different loading levels of wood.

Source	df	SS	MS	<i>F</i>	$F_{0.05, 1, 22}=4.301$
Total	7	8.57E-06			
Among	1	2.56E-06	2.56E-06	9.36892515	
Within	22	6.01E-06	2.73E-07		

Ans: $F = 9.369 > F_{0.05, 1, 22} = 4.301$, significant

Appendix: II Conference Publications

Conference papers which are not listed in the thesis:

The first paper was presented at Global Plastics Environmental Conference 2007 while the second paper was presented at Society of Plastic Engineers Annual Technical Conference 2007

Recycling ABS from End-of-Life Electronics into Wood-Plastic Composites

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Abstract

Most efforts aimed at recycling post-consumer plastics into high-value applications involve separating polymers by chemical type since the collection process necessarily results in commingled plastics, and mixed plastics have poor mechanical properties. In our prior work on acrylonitrile-butadiene-styrene (ABS), we have shown that when the impurities present in the plastic are either immiscible with it or require higher temperatures for processing, more than 99% purity is needed to prevent a very significant loss in impact strength and ductility; satisfying this extremely stringent requirement is prohibitively expensive, and alternative approaches are required. Here, we demonstrate that reinforcing recovered ABS with wood particulates is a viable method of recycling ABS from end-of-life electronics. When ABS obtained from computer monitors and keyboards was extrusion compounded with an equal amount of wood flour and appropriate additives, the measured mechanical properties were only slightly different from the corresponding properties of virgin ABS containing the same amount of wood reinforcement. Thus, the added reinforcement is able to properly mask the composition-dependent variation of mechanical properties of the base polymer.

Introduction

At least 100 billion pounds of plastics are produced in the U.S. each year, and these include such common materials as polyethylene and polypropylene. Once articles made from these polymers come to the end of their useful lives, it is desirable to reuse them in other applications. Indeed, there have been large programs directed at recycling nylon carpet fibers, polyethylene grocery bags and PET beverage bottles. The reasons for focusing on these specific polymers have been their high volumes, implying ease of collection, and the fact that they can be collected without significant contamination by other polymers; it should be noted that the presence of impurities leads to a loss of mechanical properties. However, even these efforts have been hampered by the low resale value of the recycled materials, especially in an environment where higher-quality virgin polymers are often available at a cost that is lower than the cost of collecting and reprocessing the once-used plastics.

In the present research, we have focused on recycling plastics used in electronic applications such as computer and printer housings. This is because: (i) Computers are discarded after only three or four years of use and a large amount of plastic is likely to end-up in landfills; this material may have

to be treated as hazardous waste due to contamination with heavy metals that are found in computers and computer monitors. (ii) The plastics used in electronic applications are relatively expensive polymers such as polycarbonate (PC) and ABS. Thus, attempting to recover and reuse these polymers is economically less challenging than recycling polyethylene and polypropylene. However, a variety of polymers are used to make equipment housing, and the PC or ABS obtained from post-consumer electronics is likely to be mixed with other polymers such as high-impact polystyrene (HIPS), polyvinyl chloride and polyolefins. Now, therefore, one has to deal with mixed plastics. These, unfortunately, have unacceptably poor mechanical, flow and thermal properties. In our previous work [1, 2], we made a basket of impurities containing equal amounts of PC, polyethylene, polymethyl methacrylate, polyphenylene oxide, polystyrene and polyvinyl chloride and added them to virgin ABS at the 1 wt% level. We then measured the impact strength and ductility of this contaminated ABS and found that the presence of even this tiny quantity of polymeric impurity led to ABS having large reductions in these two properties. In particular, we have found that the most damaging impurities are those that are neither miscible with the ABS nor are processable with it at the same processing temperature. As a consequence, recovered (but mixed) ABS can generally not be used to make new computer housings. All this increases the cost of recycling, and one is obliged to examine alternate approaches to the recycling of mixed plastics.

If we examine industry practice, we recognize that the products of extrusion compounding are typically filled, toughened and reinforced polymers as well as polymer blends. Here, one intentionally adds solids or other polymers to a polymer of interest to improve its properties. It, therefore, seems to us that, instead of trying to remove constituents of mixed plastics at great cost, we should add fillers or reinforcements that have the potential to mask and even overpower the composition-driven and molecular-weight driven variations in properties of the base polymer. In the present work, we show that, in the case of ABS, this is possible with the addition of wood particulates. This represents a continuation of our previous work [3] where we demonstrated that the mechanical and flow properties of recovered PC containing short glass fibers were indistinguishable from virgin PC containing the same amount of glass fibers.

Experimental Details

Maple wood flour (Maple 8010) of 80-mesh size (about 177 μm) and provided by American Wood Fiber was used in this work. Two different ABS polymers were employed: the first one was Cicolac® MG-94 (MFI = 11.7g/10 min at 230°C / 3.8kg) from GE Plastics, while the

second one was ABS recovered from end of life electronics (MFI = 3.2g/10min at 230°C / 3.8kg) and provided by SDR plastics of Millwood, WV. The mechanical properties of both the virgin and recycled materials were similar except for elongation at break and the notched Izod impact strength. The elongation at break of virgin ABS was about 52% in a tensile test while the corresponding value for the recycled ABS was only about 3%. Similarly, the notched Izod impact strength values were 216 J/m versus 88 J/m. These property differences are, no doubt, due to the presence of impurities in the polymer recovered from computer monitors and keyboards. These impurities act as stress concentrators and cause deterioration in key mechanical properties. In some of the formulations, styrene maleic anhydride, SMA 3000F ($M_n = 3800$, KOH/gm = 480) provided by Sartomer was used as a coupling agent between wood and the ABS, and, in all cases, a lubricant package, Struktol's TPW 113, was used to reduce melt fracture during extrusion; the amount of lubricant added was 5 wt% of matrix.

Wood-plastic composites containing 50 wt% wood flour were prepared using a Leistritz Micro-27 co-rotating twin-screw extruder. The wood flour was dried at 100°C for seven hours to ensure that the moisture content was less than 1wt% while the virgin or recycled ABS was dried at 85°C for 3 hours. All the ingredients were fed simultaneously to the hopper, and the processing temperature was increased from 165 to 180°C on going from the hopper to barrel 6. The temperatures of the last three barrels, though, were set at 200°C, while the die temperature was set at 220°C to reduce the severity of melt fracture. The screw speed was 200 rpm, and the total mass flow rate was 7 kg/hr. WPC strands were extruded into a water bath and were pelletized and dried before being injection molded into ASTM test specimens using a Battenfeld injection molding machine. The tensile and flexural properties of these samples were measured in accordance with ASTM D638 and D790 procedures respectively with the help of an Instron 5567 universal testing machine. The impact strength was determined according to ASTM D256 using a Satec BLI impact tester. Since WPCs have low values of impact strength in the standard Izod test, a reversed notch impact test was used. Note that a minimum of five samples were tested in each case. Also, the fracture surfaces of the WPCs obtained from tension tests were examined with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM).

Results and Discussion

Figure 1 shows the tensile strength versus amount of added coupling agent for WPCs made with both kinds of ABS resins, while Figure 2 shows the corresponding results in flexure. It is seen that, in the absence of a coupling agent, use of recycled ABS yields inferior strength values, and this is not unexpected since the recycled polymer contains impurities, and its tensile strength is lower than that of the virgin polymer. However, as the loading level of SMA increases, the tensile strength of WPCs made with both virgin and recycled ABS increases. Thus, when virgin ABS is employed, the tensile strength goes from 41.5 MPa to 48 MPa as the amount of

coupling agent increases from 0 to 10% based on the amount of wood flour. Similarly, when WPCs are formulated with recycled ABS, the tensile strength reaches 42 MPa when 10 wt% SMA is used, and this strength value is more than the 40 MPa that is characteristic of polypropylene-based WPCs containing 50wt% wood flour and 4 wt% PP-g-MA as coupling agent. The likely cause of increase in strength with added SMA is improved adhesion between wood and polymer resulting from the reaction between maleic anhydride in the coupling agent and the hydroxyl groups on the surface of cellulose, on the one hand, and the compatibility between SMA and the styrene acrylonitrile in the ABS, on the other hand [4]. A comparison of Figures 1 and 2 reveals that the behavior of flexural strength versus the amount of coupling agent used in the WPC mirrors the behavior of tensile strength. Here again, the flexural strength of WPCs made with recycled ABS can equal and even exceed the flexural strength of WPCs made with virgin polypropylene.

The real advantage of using ABS over polypropylene in formulating WPCs shows up in both the tensile and flexural moduli. This is seen in Figures 3 and 4. As is evident from Figure 3, the tensile modulus of ABS-based WPCs is around 6.5 GPa, regardless of whether virgin or recovered ABS is utilized, and it increases only slightly upon adding SMA. By comparison, the modulus of polypropylene-based WPCs containing 50wt% wood is no more than 4.5 GPa; clearly, ABS-based WPCs enjoy a 33% advantage in terms of the tensile modulus over similar PP-based WPCs. As far as the flexural modulus is concerned, the use of ABS gives values of approximately 5.7 GPa, while the corresponding value for WPCs made with polypropylene is 3.6 GPa [5]. Here the advantage exceeds 50%, and this observation is very significant because the design of WPC structures is limited by modulus and not strength.

As might be expected, WPCs formulated with virgin polymer are more ductile as compared to composites made with recycled ABS in both tension and flexure, and these data are presented in Figures 5 and 6. However, these figures reveal that the ductility values resulting from the use of virgin material are only slightly higher. This is despite the fact that the recycled polymer has an elongation-at-break of only about 3% versus about 52% for virgin ABS. In other words, the difference in brittleness between the virgin and recycled polymers is not apparent in the wood-reinforced ABS. Clearly, the added wood reinforcement is able to properly mask the composition-dependent variation of mechanical properties of the base polymer. This allows reuse of recovered ABS in high-value applications and obviates the need for polymer separation for mechanical property improvement.

The reverse notched Izod impact strength of ABS-based WPCs, as a function of added coupling agent amount, is shown in Figure 7. In absolute terms, the impact strength of ABS-based WPCs is low, and this is despite the fact that the notched impact strength of virgin ABS is more than 200 J/m. The impact strength of the WPCs, however, increases with coupling agent amount because of the improvement in ductility. In relative terms, the use of recycled polymer gives a slightly lower impact strength,

again because of lower ductility values. Thus, as in the case of ductility, large property differences (impact strength of 216 J/m versus 88 J/m) between base polymers show up as small differences in the corresponding mechanical property of the wood-reinforced ABS. Note, though, that the notched impact strength of polypropylene is an order of magnitude lower than that of ABS, but the reverse notched impact strength of polypropylene containing 50wt% wood is 80 J/m without any coupling agent and 160 J/m with the use of PP-g-MA as a coupling agent. Nonetheless, ABS-based WPCs are beginning to become commercially available, especially for indoor applications [6].

The tensile fracture surfaces of the ABS-based WPCs were observed under a scanning electron microscope, and results are shown in Figures 8 and 9. Figure 8 reveals that, even in the absence of the SMA coupling agent, fiber-matrix adhesion is good as ABS is relatively hydrophilic. The wood flour has an abundance of hydroxyl groups on the surface, and these groups take part in hydrogen bonding. As a result, wood flour tends to aggregate during compounding [7]. In the presence of the SMA coupling agent, however, the maleic anhydride groups coming from the SMA react with the hydroxyl groups, and this not only improves composite strength but also disrupts the hydrogen bonding. The changed morphology can be seen in Figure 9 where only an individual wood fiber is visible.

Summary

The primary goal of this work was to establish the beneficial effect of wood fiber addition on the mechanical properties of ABS recovered from post-consumer applications. Recycled ABS (obtained from unknown sources) contains all kinds of impurities, and it has poor and variable mechanical properties as compared to virgin ABS. This, in general, rules out the use of recovered ABS in the original application and in other high-value applications. Upon the addition of a sufficient amount of wood flour to ABS, though, it is found that the mixture mechanical properties depend primarily on the wood content and not on the mechanical and rheological properties of the matrix polymer. Thus, the mechanical properties of ABS containing 50 wt% wood reinforcement

remain essentially unchanged when the virgin ABS in the matrix is replaced by recovered ABS.

The implications of the above observations are that in order to reuse, in high-value applications, ABS recovered from post-consumer applications, it may not be necessary to separate out the polymeric impurities in order to improve and standardize mechanical properties, especially impact strength and ductility. The recovered polymer can be directly used to formulate wood-plastic composites that can compete with WPCs made with virgin ABS.

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Keywords

Acrylonitrile-butadiene-styrene, Polymer recycling, Mixed plastics, Wood-plastic composites, Mechanical properties.

Figure 1 Tensile strength of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 3 Tensile modulus of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 2 Flexural strength of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 4 Flexural modulus of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 5 Elongation at break of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 6 Flexural strain at maximum load of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 7 Reversed Izod impact strength of 50wt% wood-ABS-WPCs with different amount of SMA

Figure 8 Tensile fractured surface of 50wt% wood ABS-WPCs samples without coupling agents

Figure 9 Tensile fractured surface of 50wt% wood ABS-WPCs samples with 10wt% SMA to wood flour

Synergistic Effect of PP-g-MA and SEBS-g-MA on Polypropylene-based Wood-Plastic Composites Reinforced with Nanoclay

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Abstract

In this study, polypropylene grafted maleic anhydride (PP-g-MA) and styrene ethylene-co-butylene styrene block copolymer grafted maleic anhydride (SEBS-g-MA) were employed as coupling agents for polypropylene-based wood-plastic composites containing 50 wt% wood flour. Adding PP-g-MA to wood flour increased the tensile strength of the wood-plastic composite (WPC) by 60% and the reversed-notch Izod impact strength by 100%; the modulus remained essentially unchanged. By contrast, SEBS-g-MA had a greater effect on the impact strength but a smaller influence on the tensile strength; in addition, the modulus was reduced. On adding both PP-g-MA and SEBS-g-MA to the WPC, the impact strength increased by a factor of more than 2.5, but the tensile strength was not reduced. Since the incorporation of nanoclay increases the modulus of WPCs but decreases the impact strength, the use of all three additives affords the possibility of manufacturing WPCs with high modulus and high impact strength.

Introduction

Lumber used for residential applications such as decking is typically treated with chemicals like chromated copper arsenate (CCA) to prevent degradation. However, beginning in 2004, CCA-treated wood has been phased out of the building products market by the Environmental Protection Agency [1]. A replacement product is wood/plastic composite made by dispersing about 50 wt% wood flour into a matrix of PP, polyethylene (PE), polystyrene (PS), poly vinyl chloride (PVC), or acrylonitrile-butadiene-styrene (ABS). Since the wood content in the polymer matrix is high, the appearance of WPCs is similar to natural wood, and the preferred processing method is either profile extrusion or injection molding. Since polymers like PP are non-polar (hydrophobic) while wood particulates are polar (hydrophilic), obtaining good adhesion between wood and polymer can be a problem, and this shows up as low tensile and flexural strengths [2]. In order to improve the adhesion between wood and plastics, maleic anhydride grafted polypropylene (PP-g-MA) is generally introduced as a coupling agent in order that the anhydride groups may react with the hydroxyl groups on the surface of wood flour. Thus, the tensile and flexural strengths of WPCs are increased.

Impact strength is another key property of interest. This is because the major application of WPCs in the U.S. is decking, and inadequate impact strength can result in a catastrophic failure. In Europe, on the other hand, natural fiber composites are replacing glass fiber reinforced plastics in automotive applications [3]; this is due to ease of

recycling. Here again, mechanical property requirements include impact strength, flex modulus and ultimate strength [3]. In this study, we explore the possibility of using a combination of additives to increase the tensile strength as well as impact strength of WPCs. Note that the impact strength of PP-based WPCs is very sensitive to the wood flour content. Also, as with most semi-crystalline polymers, PP possesses pseudo-ductile characteristics [4], and, in our case it does not fracture during the unnotched Izod impact test at room temperature. Consequently, the reversed-notch Izod impact test is used, and the impact strength of PP-based WPCs drops from 250 J/m to 80 J/m in this test when the wood content is increased from 10wt% to 50wt% [5].

Toughening of WPCs, using different coupling agents, has been examined by Dalvåg et al. [6] in the past. In their results, these authors found that the addition of an elastomer provides pronounced improvement in impact strength, but this happens at the expense of the modulus. This is an expected result which is observed when a low modulus elastomer is added to composites. In this regard, SEBS-g-MA has been used as a compatibilizer and toughening agent for polymer blends containing glass fibers [4, 7-8]. In particular, it is compatible with PP, PE, and PS because it contains different moieties that make it miscible with these different polymers. Therefore, it is logical to use SEBS-g-MA as a coupling agent in PP-based WPCs. Indeed, Oksman et al. studied the effect of adding SEBS-g-MA on the properties of PE or PP based WPCs [9-12]. These and other researchers [13-15] found that the addition of SEBS-g-MA not only improved the tensile strength of WPCs, it also improved impact strength; however, the modulus decreased. According to their results for PP-based WPCs made with 40 wt% pine flour, the use of 10wt% SEBS-g-MA and 4wt% PP-g-MA resulted in 107% better notched impact strength, but the modulus decreased by 35%. Given the expensive nature of polymer additives and the reduction in modulus of WPCs upon addition of SEBS-g-MA, it is of interest to vary the amount and nature of the different additives in order to improve WPC properties while using only limited amounts of elastomers and reinforcing agents. In our previous studies, nanoclay was added to the WPCs to increase the modulus [5, 16-17]. This material did increase the modulus, but the impact strength and elongation at break were reduced. In the present work, SEBS-g-MA was introduced along with nanoclay with the expectation of increasing the impact strength without sacrificing the modulus.

Experimental Procedure

Maple wood flour (Maple 8010), of 80-mesh size (about 177 μm) was provided by American Wood Fiber, while the polymer used was BP Amoco's polypropylene

homopolymer PP1246 (melt flow index = 20g / 10min at 230°C and 2.16 kg, ASTM D1238). PP-g-MA compatibilizer used was from Chemtura; it had a molecular weight of 120,000 (g/mol) with 1.0wt% MA content. SEBS-g-MA was gifted by Kraton; it is a clear linear triblock copolymer based on styrene and ethylene/butylene, with a polystyrene content of 30% and maleic anhydride content of 2wt%. Nanomer® I.30P, an octadecylamine-modified montmorillonite clay of initial d basal spacing of 2.3 nm, was purchased from Nanocor. An antioxidant was also used at the 0.1 wt% level to prevent polymer degradation during melt compounding. It is a blend of phenol and phosphite, and it was provided by Chemtura.

WPC samples were compounded using a Leistritz Micro-27 co-rotating twin-screw extruder with K-Tron powder and pellet loss-in-weight feeders. The PP-g-MA or SEBS-g-MA pellets were hand mixed with PP pellets in a bag before loading into the feeders. The wood flour was pre-dried in an oven at 100°C for 7 hours to ensure that the moisture content was less than 1wt%, while clay was pre-dried at 80°C for at least 16 hours before compounding. The barrel temperature was controlled at 165 – 180°C from hopper to the die, while the screw rotation speed was fixed at 150 rpm. The total feeding rate was controlled at 4.8 kg/hr, and all of the samples contained 50 wt% wood flour; the experimental matrix is listed in Table 1.

The compounded WPC pellets were dried at 100°C and then injection molded using a Battenfeld injection molding machine to produce standard ASTM samples. The tensile, flexural and impact strength and stiffness properties of these samples were measured using an Instron 5567 universal testing machine and a BLI impact tester. The tensile and flexural strength were analyzed according to ASTM D638 and D790 respectively, while the impact test refers to ASTM D256. The cross sectional area of the tensile samples was 13mm x 3.2mm while the overall length of the samples was 165mm (ASTM D638, Type I). Because WPCs generally showed relatively low impact strength in the standard Izod impact test, the reversed notch impact test method was applied. The fracture surfaces of the WPCs obtained from tension tests were examined with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM).

Finally, the rate of water absorption of the WPCs was determined using a “blot and weigh” method. Three weighed samples were taken from WPCs having different amounts of SEBS-g-MA but a fixed amount of PP-g-MA to conduct this test. The typical injection-molded sample of 12.5mm x 64mm x 3.175mm was put on a tray of desiccants and dried in a vacuum oven at 80°C for 12 hours. After that, each sample was soaked in a sealed container full of distilled water and was periodically removed and weighed. The results of the water absorption tests were represented as percentage weight gained versus time of immersion.

Results and Discussion

The tensile strength and tensile modulus of WPCs containing different amounts of either PP-g-MA or SEBS-g-MA are shown in Figures 1 and 2, respectively. As can

be seen in Figure 1, the tensile strength of WPCs increased from 21.8 MPa to 38.4 MPa when the PP-g-MA loading level increased from 0wt% to 2wt%. However, there were diminishing returns on adding PP-g-MA beyond the 2 wt% level. For example, the tensile strength only increased by a further 4 MPa when the loading level of PP-g-MA was increased from 2wt% to 5wt%. Thus, the addition of 2 wt% of PP-g-MA in WPCs seems to be the optimum loading level of coupling agent necessary to provide good adhesion between PP and wood flour. The modulus of WPCs is clearly not a function of PP-g-MA content and remains essentially constant. On the other hand, as can be seen from Figure 2, the strength of WPCs first increased when 1wt% of SEBS-g-MA was added but then decreased with SEBS-g-MA loading level. This is not surprising since it is known that when elastomers are used as impact modifiers in thermoplastics, the tensile strength decreases [11]. In addition, the modulus of WPCs decreases progressively with SEBS-g-MA content. The elongation at break of WPCs with added amounts of the two coupling agents is shown in Figure 3. As expected, the elongation at break of WPCs containing SEBS-g-MA first increased at the 1wt% loading level and then leveled off at higher concentrations. The elongation at break increased with PP-g-MA loading level as well, especially when the PP-g-MA content exceeded 1 wt%. It should be noted that the elongation at break of WPCs does not increase at low PP-g-MA content. The reason for this needs to be further investigated. The impact strength of WPCs with different amounts of added PP-g-MA or SEBS-g-MA is shown in Figure 4. It is found that both PP-g-MA and SEBS-g-MA increase the reversed-notch impact strength, but SEBS-g-MA provides better impact resistance than PP-g-MA. In the case of SEBS-g-MA, 1wt% of the additive led to a more than 100% increase in impact strength, while, in the case of PP-g-MA, 2wt% of PP-g-MA gave the best enhancement in impact strength. The effect of combining the two coupling agents was studied next.

Since 2wt% of PP-g-MA provides good tensile and impact strengths, the loading level of PP-g-MA was fixed at 2wt%, and the SEBS-g-MA content was varied. The tensile properties of WPCs containing 2wt% PP-g-MA and different amounts of SEBS-g-MA are shown in Figure 5. It is seen that both the tensile modulus and the tensile strength decrease in the presence of SEBS-g-MA. The property reductions, however, are not very large. With 1wt% of added SEBS-g-MA, the tensile strength decreased by only 2%, while the tensile modulus decreased by only 4%. The reversed-notch Izod impact strength and elongation at break of these same WPCs are shown in Figure 6. By adding only 1wt% SEBS-g-MA the reversed-notch Izod impact strength increased from 153 J/m to 206 J/m (35%), while the elongation at break increased from 3.6% to almost 4% (11%). For comparison purposes, it should be noted that the reversed-notch impact strength of WPCs without any additive is 80 J/m. In the presence of 2wt% of PP-g-MA, this value increases to 153 J/m, and it further increases to 206 J/m when 1wt% of SEBS-g-MA is added to the composite. In other words, the reversed notch impact strength of WPCs increased 2.6 times when only 3wt% of a combination of the two coupling agents was added.

The results of preliminary work on the microstructure of WPCs with 1wt% SEBS-g-MA only and 1wt% SEBS-g-MA plus 2wt% PP-g-MA are shown in Figures 7 and 8 respectively. The tensile fracture surface of the sample which contains 1wt% SEBS-g-MA is shown in Figure 7. It is surprising that ductile failure was observed in some of the tensile fracture surface with only 1wt% of SEBS-g-MA. On the other hand, a typical fracture surface of sample containing 1wt% SEBS-g-MA and 2wt% PP-g-MA is shown in Figure 8. In this sample, no ductile failure was found on the fracture surface. Therefore, it can be explained from the microstructure that at the 1wt% SEBS-g-MA loading, a sample containing 2wt% PP-g-MA possesses higher modulus (3.96GPa) than samples without PP-g-MA (3.67GPa). Further work needs to be done to understand the mechanism of this phenomenon.

Turning to the rate of water absorption of WPCs, which is one of the important concerns due to the possibility of dimensional changes and the possibility of fungus attack, the results of water absorption are displayed in Figure 9. At the 2wt% PP-g-MA content, the rate of water absorption decreases with increasing amounts of added SEBS-g-MA. Thus, adding SEBS-g-MA together with PP-g-MA is beneficial as far as reducing the rate of water absorption of WPCs is concerned.

In our previous work, we had shown that the addition of nanoclay (with 3 times of PP-g-MA to clay as a dispersant plus 2wt% PP-g-MA) could increase the modulus of WPCs [16], but the impact strength and elongation at break of the composites decreased with increasing nanoclay content. Since adding 1wt% of SEBS-g-MA could increase both the elongation at break and the impact strength of WPCs significantly without decreasing the tensile modulus, it was worth seeing if adding 1wt% SEBS-g-MA to WPCs reinforced with nanoclay would improve the impact properties. These results for the mechanical properties of WPCs containing nanoclay are shown in Figures 10 – 13. As can be seen from Figures 10 and 11, adding 1wt% of SEBS-g-MA does not affect the tensile strength or modulus of WPCs. These results are consistent with the corresponding results for WPCs without nanoclay. Also, as seen in Figure 12, 1wt% of SEBS-g-MA helps increase the elongation at break of WPCs slightly but not significantly. On the other hand, Figure 13 shows that the addition of 1wt% of SEBS-g-MA increases the reversed notch Izod impact strength of WPCs. Therefore, a small amount of SEBS-g-MA could improve the impact strength of WPCs significantly without negatively affecting the other mechanical properties.

Summary

Simultaneously adding 1wt% of SEBS-g-MA and 2wt% of PP-g-MA as coupling agents to PP containing 50wt% wood flour increased the reversed-notch impact strength of the WPCs by a factor of 2.5 with only a slight decrease in the tensile modulus and tensile strength. At the same time, the rate of water absorption by the WPCs decreased slightly, and this is desirable. Finally adding 1wt% of SEBS-g-MA to WPCs containing nanoclay helped to increase the impact strength and elongation at break of the composites.

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Keywords

Wood-plastic composites, PP-g-MA, SEBS-g-MA, nanoclay, mechanical properties, polypropylene.

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Table 1 Composition of various PP/wood flour composites (numbers are percentages)

Sample Number	PP Content	PP-g-MA	SEBS-g-MA	Clay Content	Wood Content
1	50				50
2	49	1			50
3	48	2			50
4	45	5			50
5	49		1		50
6	48		2		50
7	45		5		50
8	47	2	1		50
9	46	2	2		50
10	43	2	5		50
11	43	5	1	1	50
12	39	8	1	2	50
13	27	17	1	5	50

Figure 1 Tensile Strength and tensile modulus of WPCs formulated with PP-g-MA

Figure 2 Tensile strength and tensile modulus of WPCs formulated with SEBS-g-MA

Figure 3 Elongation at break of WPCs formulated with PP-g-MA or SEBS-g-MA

Figure 4 Reversed-notch Izod impact strength of WPCs formulated with PP-g-MA or SEBS-g-MA

Figure 5 Tensile Properties of WPCs containing 2wt% of PP-g-MA and different amounts of SEBS-g-MA

Figure 6 Reversed-notch Izod Impact strength and elongation-at-break of WPCs containing 2wt% of PP-g-MA and different amounts of SEBS-g-MA

Figure 7 Tensile fracture surface of 50wt% wood WPCs containing 1wt% of SEBS-g-MA.

Figure 8 Tensile fracture surface of 50wt% wood WPCs containing 1wt% SEBS-g-MA and 2wt% of PP-g-MA

Figure 9 Rate of water absorption by WPCs containing 2wt% of PP-g-MA and different amounts of SEBS-g-MA

Figure 10 Tensile strength of WPCs reinforced with nanoclay in the presence and absence of 1wt% of SEBS-g-MA

Figure 11 Tensile modulus of WPCs reinforced with nanoclay in the presence and absence of 1wt% of SEBS-g-MA

Figure 12 Elongation-at-break of WPCs reinforced with nanoclay in the presence and absence of 1wt% of SEBS-g-MA

Figure 13 Reversed-notch Izod impact strength of WPCs reinforced with nanoclay in the presence and absence of 1wt% of SEBS-g-MA